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Supplement to

MELLOR'S COMPREHENSIVE
TREATISE ON

INORGANIC AND THEORETICAL CHEMISTRY

*Prepared under the direction
of an Editorial Board*

SUPPLEMENT II

Part I

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PREFACE

Mellor's 'Comprehensive Treatise' has long been regarded by chemists the world over as one of their most valuable sources of information. That this is still true, even though the original work was completed twenty years ago, is very clearly shown by the continuing steady demand for the book.

Nevertheless, the publishers decided that, with the vast growth of chemical knowledge, the time had now arrived when Mellor should be brought up to date. Consideration showed that to rewrite the whole work would be so vast a labour as to be inordinately costly in money and in time; moreover no such reconstruction could hope to retain or recapture that personal and individual flavour, so delightfully characteristic of the author.

Hence it appeared that the proper course would be to prepare a Supplement to the 'Comprehensive Treatise' such that the chemist seeking information in some particular field of inorganic chemistry might find all he desired to know by consulting the appropriate Volume of the original work together with the corresponding Volume of the Supplement.

The aim was, therefore, to produce the series of Supplements as quickly as possible and at a relatively low cost so that it might be possible, in the future as in the past, for the individual chemist himself to possess the Volumes dealing with fields of inorganic chemistry in which he was especially interested. To achieve this, the Editorial Board, with the support and encouragement of the publishers, resolved to distribute the task of writing among a considerable number of authors, each specially qualified to deal with his particular field, and to relieve them of much tedious labour by establishing a central bureau responsible for collecting, carding and classifying abstracts of the relevant literature. It was decided, moreover, to use as the principal initial source of information the abstracts and index of 'Chemical Abstracts', published by the American Chemical Society, since sample surveys showed that the errors and omissions thus incurred would be insignificant, and the use of these sources has enabled the Editors to reduce to a minimum the time necessarily occupied by so extensive a search for information.

The preparation of this supplementary volume has involved the study of some 21,000 abstracts; many of these have been rejected as irrelevant or unimportant but over 11,000 references have been used in the text and of these a large proportion have needed some further study of the original papers.

Although an undertaking of this magnitude naturally requires a certain uniformity of procedure in construction, the Editors have neither desired nor attempted to impose restrictions that would prevent contributors from presenting, in their own terms of detail and emphasis, a comprehensive account of advances in their respective fields. That being so, some slight duplication of recorded information is inevitable, but the Editors have felt that this repetition, if occasional and if kept within proper limits, is not altogether undesirable. The consideration, for example, of isotopy is relevant both to atomic weights and to radiochemistry, and there are many similar cases where some duplication is necessary to make separate Sections each properly complete and informative. Moreover it would be impossible, even if it were desirable, to ensure that the degree of detail in which comparable matters are discussed should be even approximately the same throughout the work and, subject to the general criterion indicated above, this matter has been left largely to the discretion of each individual contributor. The whole work may thus be regarded as an integrated series of monographs, each reflecting the judgement of its author in its emphasis, in its 'fine structure' and even in its horizon, but each interlocking with others to produce a pattern of information, selection and criticism which may serve to assess both the present valüe of the material recorded in the original Treatise and the significance of more recent and contemporary research.

References, collected at the end of each Section or sub-section, are numerically keyed to the text, and a note on each page shows where the relevant references are to be found. Thus is avoided what many, including Mellor himself, have regarded as a defect in the original Treatise. By giving the Chemical Abstracts reference as well as that to the original paper, a check is provided which may facilitate a search for additional details or avoid loss of time over an inappropriate reference. It may be noted also that the Section is the unit for enumeration of Tables and Figures.

It should here be remarked that although the objective is to make the Supplements 'comprehensive' with regard to inorganic chemistry (though not, in general, to cognate matters such, for example, as manufacturing processes or physiological properties) the references do not pretend to be exhaustive. It has been left to the judgement of authors to decide what references should be incorporated to make the work 'comprehensive' in the sense intended. Throughout, the criterion as to what should be included has been that the competent chemist, seeking information on a particular field of inorganic chemistry should, by consulting the original Volume and its Supplement, obtain a clear and reasonably complete picture of useful knowledge in that field.

Since such a picture implies an adequate background, the Editors make no apology for having deliberately strayed sometimes beyond the strict confines or inorganic chemistry to discuss cognate matters like the fluorocarbons, spectroscopy and the biological aspects of radiochemistry, and to give a general indication of the principal directions of recent advances in such fields. Whereas the original Treatise was concerned not only with inorganic chemistry but also with 'Theoretical Chemistry', it has been recognized that the latter field has so developed in the last twenty years that its inclusion in the Supplements would needlessly overburden the work. The reader desiring an exposition of some physico-chemical theory or principle is therefore referred to a standard work on this subject such as the 'Advanced Treatise on Physical Chemistry' by Professor J.R. Partington. On the other hand the present Supplements aim at presenting all the available data on the physical and physico-chemical properties of each element and compound reviewed, and in so doing an attempt has often been made to indicate the degree of importance attached to such data by the contributor.

In deciding where to deal with the salts of metals an arbitrary choice had to be made, and it seemed most convenient to follow the convention established by Mellor: the hydrides, oxides, halides, sulphides, sulphates, carbonates, nitrates and phosphates are dealt with under the metal present as the basic radical; all other salts of all the metals are dealt with under the acids from which they are derived.

This Supplement, dealing with the Halogens, includes two fields in which major developments have occurred in the last two decades: the chemistry of fluorine and the radiochemistry of the halogens. It is for this reason that fluorine chemistry has been treated very fully, including the industrial production of elementary fluorine on which all else so much depends. The Editors are greatly indebted to all the authors for their enthusiastic interest in the work and for their very loyal acceptance of the necessary editorial control, but they would record especial thanks to Mr. H.R. Leech who, writing at an early stage and extensively in a difficult field, gave them much wise and candid criticism and offered many constructive suggestions which helped to determine editorial policy and the general form of the work.

The radiochemical Sections presented special difficulties because they cover new ground, familiar to only a few, and because the literature is as yet but imperfectly indexed. Here, therefore, it was necessary to rely largely on literature surveys made by the contributors themselves and the Editors would record their indebtedness to Dr. Nicholas Miller for his valuable services in directing and co-ordinating this part of the work. It will be noted that, since its known chemistry has been elucidated wholly by the methods of radiochemistry, astatine is considered only in the radiochemical Sections.

In preparing the Index, the aim has been to make it sufficiently comprehensive and informative to permit the ready discovery of specific information without burdening it with an obscuring flood of mere 'mentions'. By omitting details to which the average reader should be sufficiently guided by more general headings, much space has been saved and it is hoped that the utility of the Index has thus been enhanced.

Though the Editors hope that the policies here outlined have produced a Supplement that will prove of real service to the general body of their fellow chemists, they have no illusion of infallibility and will welcome any criticism or suggestion that may help them in future volumes to serve yet more effectively the development and application of inorganic chemistry.

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ACKNOWLEDGMENTS

In the pursuit of knowledge a man climbs on the shoulders of his predecessors. In the presentation of the results of that pursuit the Editors have endeavoured to ensure that the sources of the knowledge are clearly disclosed, and they welcome this opportunity to acknowledge their indebtedness to all the authors, reviewers and abstractors of scientific papers whose work has contributed directly or indirectly to the preparation of this Supplement. In particular they express their thanks for generous assistance afforded by Professor Glenn T. Seaborg who permitted them to make use of the Table of Isotopes compiled by J.M. Hollander, I. Perlman and G.T. Seaborg and published by the U.S. Atomic Energy Commission (page 970); by Messrs. John Wiley and Sons, Inc. in allowing them to reproduce Tables of Isotopic Exchange Reactions (page 1028); and by Imperial Chemical Industries Ltd. who have placed valuable facilities for the study and presentation of published information at the command of certain contributors.

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Page 21, fig. 3; page 23, fig. 4; page 25, fig. 5; page 104, fig. 3; page 188, fig. 1; page 422, fig. 1; page 480, fig. 1; page 587, fig. 2; page 925, fig. 2 from the *Journal of the American Chemical Society*, published by that Society. Page 31, fig. 10; page 33, fig. 11; page 35, fig. 12; page 178, fig. 3; the diagram on page 296; page 363, figs. 2 and 3; page 399, fig. 7 from *Industrial and Engineering Chemistry*, published by the American Chemical Society. Page 20, fig. 2 from the *Transactions of the Electrochemical Society*, published by the Electrochemical Society (America). Page 28, fig. 7 from *Chemische Fabrik* published by Verlag Technik G.m.b.H., Berlin. Page 29, fig. 8 from *Comptes rendus hebdomadaires des Seances de l'Academie des Sciences*, published by Gauthier-Villars, Paris. Page 30, fig. 9 from *Zeitschrift für anorganische Chemie*, published by J.A. Barth, Leipzig. Page 95, fig. 2 from *Zeitschrift für physikalische Chemie*, published by Akademische Verlagsgesellschaft Geest u. Portig K.-G., Leipzig. Page 108, fig. 5 from *Chemical Engineering*, published by the McGraw Hill Publishing Co., New York. Page 166, fig. 2 from the *Journal of the Chemical Society*, published by that Society. Page 189, fig. 2 from *Inorganic Syntheses*, published by the McGraw Hill Book Co., Inc. Page 231, fig. 6, from *Journal of Chemical Physics*, published by the American Institute of Physics. Page 276, fig. 1 from *Transactions of the American Institute of Chemical Engineers*, published by that Institute. Page 294, fig. 2 from *Journal of Chemical Education*, published by the American Chemical Society. Page 332, fig. 1 from *Chemical Reviews*, published for the American Chemical Society by Williams and Wilkins Co., Baltimore. Page 369, fig. 4 from *Acta Litterarum ac Scientiarum Regiae Universitatis Hungaricae Francisco-Josephinae*, by permission of Dr. A. Kiss. Page 376, fig. 5 and page 376, fig. 6 from *Receuil des travaux chimiques des Pays-Bas*, published by the Nederlandsche Chemische Vereeniging. Page 399, fig. 8 from *Chemical Engineering Progress*, published by the American Institute of Chemical Engineers. Page 407, fig. 1 from *Chemistry and Industry*, published by the Society of Chemical Industry. Page 546, fig. 1; page 653, fig. 4; page 654, fig. 5; page 783, fig. 3 from *Transactions of the Faraday Society*, published by that Society. Page 629, fig. 1;

page 782, fig. 2; page 915, fig. 1 from *Helvetica Physica Acta*, published by Verlag Birkhauser A.G., Basel. Page 793, fig. 4; page 931, fig. 3 from *Annales de Physique*, published by Librairie Masson et Cie., Paris. Page 37, fig. 13 and page 38, fig. 14 from *British Intelligence Objectives Survey Report*, published by H.M. Stationery Office. Page 1086, fig. 1 from *Radiochemical Studies: The Fission Products*, published by McGraw Hill Book Co., Inc. Page 430, fig. 1 from *Harwell Memorandum, A.E.R.E., 1/M 777*, (Crown Copyright) by permission of the Controller of H.M. Stationery Office. Page 41, fig. 15 from *B.P. 642,812* and page 155, fig. 1 from *B.P. 665,253*, by permission of the Controller of H.M. Stationery Office.

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ABBREVIATIONS

absolute	abs.
alternating current	a.c.
ampère	amp.
Angstrom unit	A
atmosphere-s (after a numeral)	atm.
atomic weight	at.wt.
boiling point	b.p.
British thermal unit	B.Th.U.
Calorie (large)	kg.-cal.
calorie (small)	g.-cal.
centimetre	cm.
cubic centimetre	c.c.
density (with a numeral)	ρ,d.
direct current	d.c.
electromotive force	e.m.f.
foot, feet	ft.
freezing point	f.p.
gram-s (with a numeral)	g.
hour-s (with a numeral)	hr.
inch-es	in.
kilogram	kg.
kilowatt	kW
litre-s (with a numeral)	l.
melting point	m.p.
milliampere-s	ma.
millilitre-s	ml.
millivolt-s	mV.
minute-s	min.
molecular weight	mol.wt.
parts per million	p.p.m.
potential difference	p.d.
second-s (time only)	sec.
specific gravity	sp.gr.
square centimetre-s	sq.cm.
vapour density	v.d.
vapour pressure	v.p.
volt-s	V.
watt-s	W.
wave-length	λ

LIST OF LITERATURE ABBREVIATIONS

For uniformity, the literature abbreviations used in the references are the same as in *An Advanced Treatise on Physical Chemistry* by J. R. Partington. Where a source is cited which does not appear in that work, the abbreviation is that currently used by Chemical Abstracts.

Aarsberetning vedkommende Norges Fiskerier. Oslo.

Abhl. Akad. Munich. Abhandlungen der mathematisch-physikalischen Klasse der Königlich Bayerischen Akademie der Wissenschaften. Munich.

Abhl. Ges. Wiss. Gött. Abhandlungen der Königlichen Gesellschaft der Wissenschaften zu Göttingen. Mathematisch-physikalische Klasse. Göttingen.

Abhl. K. Akad. Berlin. Abhandlungen der Kgl. Akademie der Wissenschaften zu Berlin. Physikalisch-mathematische Klasse. Berlin.

Abhl. Naturwiss. Verein Hamburg. Abhandlungen aus dem Gebiete der Naturwissenschaften. Herausgegeben vom Naturwissenschaftlichen Verein in Hamburg. Hamburg.

Abhl. Sächs. Akad. Abhandlungen der Königlich Sächsischen Akademie der Wissenschaften zu Leipzig. Mathematisch-physische Klasse. Leipzig.

Abstr. Roy. Soc. Abstracts of Papers Communicated to the Royal Society of London. London.

Acta Acad. Aboensis Math. Phys. Acta Academiae Aboensis, Mathematica et Physica. Abo, Finland.

Acta Adriat. Acta Adriatica. Split, Yugoslavia.

Acta Chem. Scand. Acta Chemica Scandinavica. Copenhagen.

Acta Comment. Univ. Dorpatensis. Acta et Commentationes Universitatis Dorpatensis. Dorpat (Yuriev or Jurjeff).

Acta Cryst. Acta Crystallographica. London.

Acta Lit. Sci. Reg. Univ. Hung. Acta Litterarum ac Scientiarum Regiae Universitatis Hungaricae Francisco-Josephinae. Szeged, Hungary.

Acta Math. Acta Mathematica. Stockholm.

Acta Med. Scand. Acta Medica Scandinavica. Stockholm.

Acta Phys. Hungar. Acta Physica Academiae Scientiarum Hungaricae. Budapest.

Acta Phys. Polon. Acta Physica Polonica. Warsaw.

Acta Physicochim. U.R.S.S. Acta Physicochimica U.R.S.S.

Acta Soc. Sci. Fenn. Acta Societatis Scientiarum Fennicae. Helsingfors.

Acta Univ. Asiae Mediae. Acta Universitatis Asiae Mediae. Tashkent.

Acta Univ. Latviensis. Acta Universitatis Latviensis. Riga.

Acta Univ. Szeged, Chem et Phys. Acta Universitatis Szegediensis, Sectio Scientiarum Naturalium, Acta Chemica et Physica.

Acta Univ. Voron. Acta Universitatis Voronegiensis.

Adv. in Chem. Advances in Chemistry Series.

A.E.C.D. Atomic Energy Commission Documents.

A.E.R.E., Reports. Atomic Energy Research Establishment, Reports.

Agr. & Live-stock in India. Agriculture and Live-stock in India.

Aircraft Eng. Aircraft Engineering. London.

Akust. Z. Akustische Zeitschrift. Leipzig.

Alembic Club Reprint. Alembic Club Reprints. Edinburgh.

Allg. Brauer u. Hopfenzeit. Allgemeine Brauer- und Hopfenzeitung.
Allg. Öl u. Fettztg. Allgemeine Öl- und Fettzeitung. Vienna.
Aluminium Non-Ferrous Rev. Aluminium and the Non-Ferrous Review. London.
Amer. Chem. Abstr. Chemical Abstracts. Published by the American Chemical Society. Easton, Pa.
Amer. Chem. J. American Chemical Journal. Baltimore.
Am. Dyestuff Reptr. American Dyestuff Reporter. New York.
Amer. Gas J. American Gas Journal. New York.
Amer. Inst. Min. Met. Eng. Contrib. American Institute of Mining and Metallurgical Engineers. Contributions. New York.
Amer. Inst. Min. Met. Eng. Techn. Publ. American Institute of Mining and Metallurgical Engineers. Technical Publication. New York.
Amer. Inst. Min. Met. Eng. Met. Div. Techn. Pub. American Institute of Mining and Metallurgical Engineers. Metallurgical Division. Technical Publication. [Journal of Metals]. New York.
Amer. J. Botany. American Journal of Botany. Maryland.
Amer. J. Clin. Pathol. American Journal of Clinical Pathology. Baltimore.
Amer. J. Dental Res. American Journal of Dental Research. Chicago.
Amer. J. Hyg. American Journal of Hygiene. Baltimore.
Amer. J. Math. American Journal of Mathematics. Pure and Applied. Baltimore.
Amer. J. Med. Sci. American Journal of the Medical Sciences. Philadelphia.
Amer. J. Orthodontics etc. American Journal of Orthodontics and Oral Surgery.
Amer. J. Pharm. American Journal of Pharmacy. Philadelphia.
Amer J. Phys. American Journal of Physics. Lancaster.
Amer. J. Pub. Health. American Journal of Public Health.
Amer. J. Roentgen. American Journal of Roentgenology. Oxford.
Amer. J. Sci. American Journal of Science. New Haven, Conn.
Amer. J. Surg. American Journal of Surgery. New York.
Amer. J. Trop. Med. American Journal of Tropical Medicine. Baltimore.
Amer. Machinist. American Machinist. New York. [Also a London edition, with supplement].
Amer. Min. The American Mineralogist. Princeton, New Jersey.
Amer. Scientist. American Scientist. Burlington, New Jersey.
American Scientist. The Sigma Xi Quarterly. New Haven, Conn. (Harvard University).
Amer. Soc. Refrig. Eng. J. American Society of Refrigerating Engineers Journal. New York.
Amer. Soc. Testing Mat. Bull. American Society for Testing Materials. Bulletin. Easton, Pa.
Amer. Soc. Testing Mat. Radiography Symposium. American Society for Testing Materials. Symposium on Radiography and *X*-Ray Diffraction Methods. Philadelphia, 1937.
An. Acad. Brasil. Cienc. Anais Academia Brasileira de Ciencias. Rio de Janeiro.
An. Acad. Roman. Mem. Sti. Analele Academiei Române. Memorie Sect. Stientifice. Bucarest.
An. Asoc. Quim. Argentina. Anales de la Associación Quimica Argentina. Buenos Aires.
An. Asoc. Quim. Farm. Uruguay. Anales de la Asociación de Quimica y Farmacia del Uruguay. Montevideo.
An. Assoc. Quim. Brasil. Anais de Associacão Quimica de Brasil. São Paulo.
An. Fac. Farm. Odont. Anais de faculdade de farmácia e odontologia da universidade de São Paulo. São Paulo.

An. Facult. Quim. Farm. Anales .de la Facultad de Quimica y Farmacia. Montevideo.
An. Farm. Bioquim: Anales de Farmacia y Bioquimica. Buenos Aires.
An. Fis. Quim. Anales de la Real Sociedad Española de Fisica y Quimica. Madrid. [Now divided into A, Physics and B, Chemistry].
An. Quim. Farm. Anales de Quimica y Farmacia. Santiago, Chile.
An. Real. Acad. Farm. Anales de la Real Academia de Farmacia. Madrid.
An. Soc. Cient. Argentina. Anales de la Sociedad Cientifica Argentina. Buenos Aires.
An. Soc. Españ. Fis. Quim. Anales de la Sociedad Española de Fisica y Quimica. Madrid.
Anal. Chem. See *Ind. Eng. Chem. Anal.*
Anal. Chim. Acta. Analytica Chimica Acta. Houston, Tex., London, Amsterdam.
Analyst. The Analyst. London.
Angew. Bot. Angewandte Botanik. Berlin-Zehlendorf.
Angew. Chem. Angewandte Chemie. Sections A and B. Leipzig.
Anilinokrasochnaya Prom. Anilinokrasochnaya Promyshlennost.
Ann. Annalen der Chemie. [Liebig's Annalen]. Leipzig.
Ann. Acad. Sci. Fenn. Annales Academiae Scientiarum Fennicae. Helsingfors.
Ann. Appl. Biol. Annals of Applied Biology. London.
Ann. Astrophys. Annales d'astrophysique. Paris.
Ann. Chim. Annales de Chimie. Paris. [Formerly combined with Annales de Physique as Annales de Chimie et de Physique].
Ann. Chim. Anal. Appl. Annales de Chimie Analytique et de Chimie Applique. Paris.
Ann. Chim. Appl. Annali di Chimica Applicata. Rome.
Ann. de l'École Norm. Annales Scientifiques de l'École Normale Superieure. Paris.
Ann. de Phys. Annales de Physique. Paris. [See *Ann. Chim.*].
Ann. Dermatol. Syphil. Annales de Dermatologie et de Syphiligraphie. Paris.
Ann. des Ponts et Chaussées. Annales des Ponts et Chaussées. Paris.
Ann. Entomol. Soc. Amer. Annals of the Entomological Society of America. Columbus, Ohio.
Ann. Ergzb. Annalen der Chemie Ergänzungsbände. [See *Ann.*].
Ann. Fac. Sci. Toulouse. Annales de la Faculté des Sciences de Toulouse. Toulouse.
Ann. Fals. Annales des Falsifications et des Fraudes. Paris.
Ann. Inst. Anal. Phys. Chim. Annales de l'Institut d'Analyse Physicochimique. Moscow.
Ann. Intern. Med. Annals of Internal Medicine. Philadelphia.
Ann. Mat. Pura ed Applicata. Annali di Mathematica Pura ed Applicata. Milan, Bologna.
Ann. Med. Leg. Crim. Police Sci. Med. Soc. Toxicol. Annales de Médecine Légale de Criminologie, Police Scientifique, Médecine Sociale et Toxicologie. Paris.
Ann. Mines. Annales des Mines. Paris. [A continuation of Journal des Mines].
Ann. New York Acad. Sci. Annals of the New York Academy of Sciences. New York.
Ann. Pharm. Franc. Annales Pharmaceutiques Françaises. Paris.
Ann. Phil. Annals of Philosophy. London.
Ann. Phys. Annalen der Physik. Leipzig. [Several series, each with a separate volume number sequence; formerly Annalen der Physik und Chemie, etc. Sometimes quoted as Poggendorff's Annalen, Wiedemann's Annalen, Drude's Annalen, with the name of the Editor].

Ann. Phys. Beibl. Beiblätter zu den Annalen der Physik (1881–1919). Leipzig. [Continued as *Phys. Ber.*].

Ann. Phys. Boltzmann Festschr. Ludwig Boltzmann Festschrift Gewidmet. Leipzig, 1904. [Uniform with the volumes of Annalen der Physik].

Ann. Phys. Ergzb. Annalen der Physik Ergänzungsbände. [See *Ann. Phys.*].

Ann. Phys. Pogg. Jubelband. Annalen der Physik. Poggendorff Jubelband. Berlin, 1874. [See *Ann. Phys.*].

Ann. Rept. Intern. Assoc. Milk Sanitarians. Annual Report of the International Association of Milk Sanitarians.

Ann. Rep. Chem. Soc. Annual Reports of the Chemical Society. London.

Ann. Rep. Smithsonian Inst. Smithsonian Institute Reports. Washington.

Ann. Rev. Biochem. Annual Review of Biochemistry. Stanford, U.S.A.

Ann. Rev. Phys. Chem. Annual Review of Physical Chemistry. Stanford, U.S.A.

Ann. Sci. Univ. Jassy. Annales Scientifique de l'Université de Jassy. Jassy, Rumania.

Ann. Sect. Anal. Phys. Chim. Inst. Chim. Gén. U.R.S.S. Annales du Secteur d'Analyse Physico-Chimique. Institut de Chimie Générale, U.R.S.S. Moscow.

Ann. Soc. Sci. Bruxelles. Annales de la Société Scientifique de Bruxelles. Louvain, Belgium.

Ann. Univ. Sofia [phys. math.]. Annuaire de l'Université de Sofia. Faculté Physico-Mathematique. Sofia.

Annali di Chimica. Annali di Chimica e Storia Naturali. Pavia.

Annals of Sci. Annals of Science. London.

Anz. Schädlingskunde. Anzeiger für Schädlingskunde. Berlin.

Apotheker Ztg. Apothekerzeitung. Berlin.

Appl. Sci. Res. Applied Scientific Research. Section A. The Hague, Holland.

Arb. dritt. Abt. anat. Inst. kaiser. Univ. Kyoto. Arbeiten aus der dritten Abteilung des anatomischen Institutes der kaiserlichen Universität Kyoto.

Arb. K. Wilhelm Inst. Kohlenforsch. Arbeiten. Kaiser-Wilhelm Institut für Kohlenforschung in Mühlheim-Ruhr. Berlin.

Arb. Kais. Ges. Arbeiten aus dem kaiserlichen Gesundheitsamte.

Arb. Reichsgesund. Arbeiten aus dem Reichsgesundheitsamte.

Arch. Biochem. Archives of Biochemistry. New York.

Arch. di Fisiol. Archivio di Fisiologia. Florence.

Arch. Eisenhüttenw. Archiv für das Eisenhüttenwesen. Düsseldorf.

Arch. Exp. Path. Pharm. Archiv fur experimentelle Pathologie und Pharmakologie. Leipzig.

Arch. Farm. Bioquim. Tucumán. Archivos de Farmacia y Bioquimica del Tucumán. Tucumán, Argentina.

Arch. Ges. Physiol. (Pflüger). Pflüger's Archiv für die gesamte Physiologie des Menschen und der Tiere. Berlin.

Arch. Ges. Virusforsch. Archiv für die gesamte Virusforschung. Vienna.

Arch. Intern. Pharmacod. Archives Internationales de Pharmacodynamie et de Thérapie. Ghent, Belgium.

Arch. Ist. Biochim. Ital. Archivio dell'Istituto Biochimico Italiano.

Arch. Lagerstättenforsch. Archiv für Lagerstättenforschung. Berlin.

Arch. Mat. Naturvidensk. Archiv for Mathematik og Naturvidenskab. Oslo.

Arch. Med. Interna. Havana. Archivos de Medicina Internale. Havana.

Arch. Metallkde. Archiv für Metallkunde. Berlin.

Arch. Min. Soc. Sci. Varsovie. Archives de Mineralogie de la Société des Sciences de Varsovie. Warsaw.

Arch. Mus. Teyler. Archives du Musée Teyler. Haarlem.

Arch. Néerl. Archives Néerlandais des Sciences Exactes et Naturelles. (Sciences Exactes). The Hague, Holland.

Arch. Otolaryngol. Archives of Otolaryngology. Chicago.

Arch. Pharm. Archiv der Pharmazie. Leipzig.

Arch. Pharm. Chemi. Archiv for Pharmaci og Chemi. Copenhagen.

Arch. Physiol. Archives de Physiologie Normale et Pathologique. Paris.

Archives Internationales de Physiologie. Paris.

Arch. Phys. Biol. Archives de Physique Biologique. Paris.

Arch. Sci. Biol., Italy. Archivio di Scienze Biologiche (Italy). Bologna.

Arch. Sci. Biol. U.R.S.S. Archives des Sciences Biologiques. Petrograd.

Arch. Sci. Phys. Nat. Archives des Sciences Physiques et Naturelles. Geneva.

Arch. Sci. Physiol. Archives des Sciences Physiologiques. Paris.

Arch. techn. Messen. Archiv für technisches Messen. Munich.

Arch. Wärmewirtsch. Archiv für Wärmewirtschaft. Berlin.

Archiv Gesch. Naturwiss. Technik. Archiv für die Geschichte der Naturwissenschaft und der Technik. Leipzig.

Arhiv Hem. Farm. Arhiv za Hemiju i Farmaciju. Zagreb, Yugoslavia.

Arhiv Kem. Arhiv za Kemiju. Zagreb, Yugoslavia.

Arkiv Fys. Arkiv för Fysik. Stockholm.

Arkiv Kem. Arkiv för Kemi. Uppsala, Stockholm.

Arkiv Kem. Min. Geol. Arkiv för Kemi, Mineralogi och Geologi. Stockholm.

Arkiv Mat. Astron. Fys. Arkiv för Matematik, Astronomi och Fysik. Stockholm.

Army Ordnance. Washington.

Assoc. Food Drug Officials U.S. Quart. Bull. Association of Food and Drug Officials of the United States. Quarterly Bulletin. Topeka.

Assoc. Operative Millers. Association Operative Millers, Bulletin. Kansas City.

Astron. J. Astronomical Journal. Albany, U.S.A.

Astrophys. J. The Astrophysical Journal. Chicago.

Ateneo Parmense. Parma.

Atti Accad. Catania. Atti della R. Accademia Gioenia di Scienze Naturali. Catania.

Atti Accad. Ital. Fis. Mat. Atti della Reale Accademia d'Italia. Memorie della Classe di Scienze Fisiche, Matematiche e Naturali. Rome.

Atti Congr. Naz. Chim. Pura Applic. Atti del Congresso Nazionale di Chimica Pura ed Applicata. Rome.

Atti R. Accad. Lincei. Atti della Reale Accademia dei Lincei. Rendiconti. Classe di Scienza Fisiche, Matematiche e Naturali. Rome.

Atti R. Accad. Napoli. Atti della Reale Accademia delle Scienze Fisiche e Matematiche. Societa Reale di Napoli. Naples.

Atti R. Accad. Torino. Atti della Reale Accademia delle Scienze di Torino. Turin.

Atti R. Inst. Veneto. Atti del Reale Instituto Veneto di Scienze, Lettere ed Arti. Venice.

Atti Regia Accad. Fisiocrit. Siena, Sez. Atti della Regia Accademia dei Fisiocritici in Sciena, Sezione Medico-Fisica. Siena.

Australian J. Exp. Biol. Med. Sci. Australian Journal of Experimental Biology and Medical Science. Adelaide.

Australian J. Sci. Australian Journal of Scientific Research. Series A. Physical Sciences. East Melbourne.

Avhl. Norsk. Videns. Akad. Oslo. Avhandlingen uitgitt av det Norske Videnskaps-Academie i Oslo. I. Matematisk-Naturvidenskapelig Klasse. Oslo.

Azerbaid. Neft. Khozy. Azerbaidzhanskoe Neftyanoe Khozyaistvo. Baku, U.S.S.R.

B.A.E.R. British Atomic Energy Reports.

B.A. Rep. British Association for the Advancement of Science. Reports. London.

B.A. Rep. Coll. Chem. Reports on Colloid. Chemistry. British Association for the Advancement of Science. London.
B.P. British Patent.
Bauing. Der Bauingenieur. Berlin.
Beiheft. Z. v. deut. Chem. Zeitschrift des Vereins deutscher Chemiker (Beiheft). [Formerly Zeitschrift für Angewandte Chemie].
Beitr. Geophys. Gerlands Beiträge zur Geophysik. Leipzig.
Beitr. Kryst. Min. Beiträge zur Krystallographie und Mineralogie. Heidelberg.
Beitr. Min. Petr. Beiträge zur Mineralogie und Petrographie. Heidelberg.
Bell Lab. Rec. Bell Laboratories Record. New York.
Bell Syst. Techn. J. Bell System Technical Journal. New York.
Bell Telephone Syst. Techn. Monogr. Bell Telephone System Technical Monographs. New York.
Bell Telephone Syst. Techn. Publ. Bell Telephone System Technical Publications. New York.
Ber. Berichte der Deutschen chemischen Gesellschaft. Berlin.
Ber. D. keram. Ges. Berichte der Deutschen keramische Gesellschaft. Berlin.
Ber. D. Phys. Ges. See *Z. Phys.*
Ber. Inst. Phys. Chem., Akad. Wiss. U.S.S.R. Berichte des Instituts für physikalische Chemie, Akademie der Wissenschaften der U.S.S.R. Kiev.
Ber. Nat. Med. Verein. Innsbruck. Berichte des naturwissenschaftlich-medizinischen Vereins in Innsbruck. Innsbruck.
Ber. Oberhess. Ges. Natur- u. Heilkde. Bericht der Oberhessischen Gesellschaft für Natur- und Heilkunde. Giessen.
Ber. Phys.-ökonom. Ges. Königsberg. Bericht uber die in den Sitzungen der Physikalisch-ökonomischen Gesellschaft zu Königsberg in Pr. gehaltenen Vorträge. Königsberg.
Ber. Verhl. Nat. Ges. Freiburg. Berichte über die Verhandlungen der Naturforschende Gesellschaft zu Freiburg i. Br. Freiburg.
Beret. 18th Skand. Naturforskermode. Beretning om det Skandinaviske Naturforskermode. 18th meeting, Copenhagen, 1929.
Berg. u. Hütten. Monatsh. Berg- und hüttenmännische Monatshefte der montanistischen Hochschule in Leoben. Vienna.
Bergm. J. Bergmännische Journal. Freiberg.
Berl. u. Münch. Tier. Woch. Berliner und Münchener tierärztliche Wochenschrift. Berlin-Friedenau.
Berlin Ber. Sitzungsberichte der [Königlich] Preussischen Akademie der Wissenschaften. Physikalisch-Mathematische Klasse. Berlin.
Berlin. klin. Wochenschr. Berliner klinische Wochenschrift. Berlin.
Bibl. Univ. Bibliothèque Universelle de Genève. Geneva.
Biedermann's Zentr. Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschaft. Berlin, Leipzig.
Bihang Kgl. Svensk. Vet. Akad. Handl. Bihang till Kongliga Svenska Vetenskaps-Akademiens Handlinger. Stockholm.
Biochem. J. The Biochemical Journal. Liverpool.
Biochem. Z. Biochemische Zeitschrift. Berlin.
Biochim. & Biophys. Acta. Biochimica et Biophysica Acta. Amsterdam.
Biochim. Terap. Biochimica e Terapia Sperimentale. Milan.
Biodynamica. St. Louis, Missouri.
Biokhimiya. Moscow, Leningrad.
Bodenkunde u. Pflanzenernähr. Bodenkunde und Pflanzenernährung.
Bol. Acad. Cienc. Argentina. Boletin de la Academia Nacional de Ciencias de la Republica Argentina. Córdoba.
Bol. Acad. Cienc. Exactas (Mad). Boletin de la Academia de Ciencias Exactas, Fisicas y Naturales (Madrid).

Bol. Assoc. Brasil. Met. Boletim da Associação Brasiliera de Metais. São Paulo.

Bol. Inst. Españ. Oceanog. Boletin del Instituto Español de Oceanografia. Madrid.

Bol. Obras. Sanit. Nacion. Boletin de Obras Sanitarias de la Nación. Buenos Aires.

Bol. Ofic. Asoc. Tecn. Cuba. Boletin Oficial del Asociación de Técnicos Azucareros. Cuba.

Bol. Soc. Ital. Biol. Speri. Bolletino della Societa Italiana de Biologia Sperimentale. Naples.

Bol. Soc. Quim. Peru. Boletin de la Sociedad Quimica del Peru. Lima, Peru.

Boll. Accad. Catania. Bolletino delle Sedute dell'Accademia Gioena di Scienze Naturali in Catania. Catania.

Boll. Chim. Farm. Bolletino Chimico Farmaceutico. Milan.

Boll. Oculist. Bolletino d'Oculistica. Bologna, New York.

Boll. Sci. Fac. Chim. Ind. Bologna. Bolletino Scientifico della Facoltà di Chimica Industriale dell'Università di Bologna. Bologna.

Boll. Soc. Geol. Ital. Bolletino della Società Geologica Italiana. Rome.

Boll. Staz. Pato. Vegetale. Bolletino della Stazione di Patologia Vegetale. Rome.

Braunkohle. Halle.

Brennstoff. Chem. Brenstoff-Chemie. Essen.

Brennstoff- u. Wärmewirtsch. Brennstoff und Wärmewirtschaft. Berlin.

Brit. Chem. Abstr. British Abstracts. Bureau of Abstracts. London.

Brit. Clayworker. The British Clayworker. London.

Brit. J. Exp. Path. British Journal of Experimental Pathology. London.

Brit. J. Ophthalmol. British Journal of Ophthalmology. London.

Brit. J. Radiol. British Journal of Radiology. London.

Brit. Med. J. British Medical Journal. London.

Brit. Stand. Specif. British Standard Specification. British Standards Institution. London.

Brown Boverie Rev. Brown Boverie Review. Baden.

B.S.I. British Standards Institution. London.

Bul. Fac. Stiinte Cernăuti. Buletinul Facultăţii de Stiinte din Cernăuti.

Bul. Sci. Fak. Terkultura. Bulteno Scienca de la Fakultato Terkultura, Kjusu Imperia Universitato, Fukuoka, Japanujo.

Bul. Soc. Chim. Roman. Buletinul Societatii de Chimie (din Romania). Bucarest.

Bul. Soc. Român. de Stiinte. Buletinul de Chimie Pură si Applicată, Societatea Română de Stiinte. Bucarest.

Bul. Soc. Stiinte Cluj. Buletinul Societătii de Stiinte din Cluj. Cluj, Rumania.

Bul. Soc. Stiinte Farm. Roman. Buletinul de Societătii Stiinte e Farmacia Romane.

Bul. Stiinte Fiz. Soc. Română Stiinte. Buletinul de Stiinte Fizica Pure si Aplicate, Societatea Română de Stiinte.

Bull. Acad. Med. Bulletin de l'Académie de Médecine. Paris.

Bull. Acad. Polon. Bulletin Internationale de l'Académie Polonaise des Sciences et Lettres. Section A. Cracow.

Bull. Acad. Romaine. Bulletin de la Section Scientifique de l'Academie Roumaine.

Bull. Acad. Roy. Belg. Bulletin de l'Académie Royale de Belgique. Classe des Sciences. Brussels.

Bull. Acad. Sci. Georgian S.S.R. Bulletin of the Academy of Sciences of the Georgian S.S.R.

Bull. Acad. Sci. Russe. Bulletin de l'Academie des Sciences de Russie. Petrograd.

Bull. Acad. Sci. (U.P.) Agra & Oudh. Bulletin of the Academy of Sciences of the United Provinces of Agra and Oudh, Allahabad, India.

Bull. Acad. Sci. U.R.S.S. Bulletin de l'Academie des Sciences de l'Union des Republiques Sovietiques Socialistes.

Bull. Acad. St. Petersb. Bulletin de l'Academie Imperiale des Sciences de St. Petersburg. St. Petersburg.

Bull. Amer. Ceram. Soc. Bulletin of the American Ceramic Society. Columbus, Ohio.

Bull. Assoc. Chim. Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie de France et des Colonies. Paris.

Bull. Biol. Med. Exptl. U.R.S.S. Bulletin de Biologie et de Medecine Experimentale de l'U.R.S.S.

Bull. Brit. Soc. Hist. Sci. Bulletin of the British Society for the History of Science. London.

Bull. Chem. Soc. Japan. Bulletin of the Chemical Society of Japan. Tokyo.

Bull. Comm. Geol. Finlande. Bulletin de la Commission Geologique de Finlande. Helsinki.

Bull. Ecole Polytechn. Jassy. Bulletin de l'Ecole Polytechnique de Jassy. Jassy, Rumania.

Bull. Eng. Expt. Stat. Univ. Illinois. University of Illinois. Engineering Experiment Station. Bulletin. Urbana, Ill.

Bull. Geol. Inst. Manchoukuo. Bulletin of the Geological Institute of Manchoukuo..

Bull. Geol. Soc. Amer. Bulletin of the Geological Society of America. New York.

Bull. Imp. Inst. Bulletin of the Imperial Institute.

Bull. Inst. Internat. Froid. Bulletin. Institut Internationale du Froid. Paris.

Bull. Inst. Min. Met. Bulletin of the Institution of Mining and Metallurgy. London.

Bull. Inst. Phys. Chem. Res. Tokyo. Bulletin of the Institute of Physical and Chemical Research. Tokyo.

Bull. Inst. Polyt. Ivanovo-Vosniesensk. Bulletin de l'Institut Polytechnique a Ivanovo-Vosniesensk.

Bull. Intern. Acad. Polonaise. Bulletin Internationale de l'Academie Polonaise des Sciences et des Lettres. Cracow, Poland.

Bull. Johns Hopkins Hosp. Bulletin of the Johns Hopkins Hospital. London, Baltimore.

Bull. Minnesota Univ. Eng. Expt. Stat. Engineering and Experimental Station Bulletin. University of Minnesota. Minneapolis.

Bull. Nat. Formulary Comm. Bulletin of the National Formulary Committee. Washington.

Bull. Nat. Res. Counc. Bulletin of the National Research Council. Washington.

Bull. Offic. Direction Rech. Sci. Ind. Inventions. Bulletin Official de la Direction des Recherches Scientifiques et Industrielles et des Inventions.

Bull. Rubber Growers' Assoc. Bulletin of the Rubber Growers' Association. London.

Bull. Sci. Acad. Roy. Belg. See *Bull. Acad. Roy. Belg.*

Bull. Sci. Pharmacol. Bulletin des Sciences Pharmacologiques. Paris.

Bull. Sect. Sci. Acad. Roum. Bulletin de la Section Scientifique de l'Academie Roumaine. Bucarest.

Bull. Soc. Chim. Bulletin de la Societe Chimique de France. Paris.

Bull. Soc. Chim. Belg. Bulletin de la Societe Chimique de Belgique. Brussels.

Bull. Soc. Chim. Belgrade. Bulletin de la Societe Chimique Belgrade. Belgrade.

Bull. Soc. Chim. Biol. Bulletin de la Société de Chimie Biologique. Paris.
Bull. Soc. Encourag. Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Paris.
Bull. Soc. Franc. Elec. Bulletin de la Société Française des Électriciens. Seine, France.
Bull. Soc. Franc. Min. Bulletin de la Société Française de Minéralogie. Paris.
Bull. Soc. Geol. Bulletin de la Société Géologique de France. Paris.
Bull. Soc. Ind. Min. Bulletin de la Société de l'Industrie Minérale de St. Étienne. Paris.
Bull. Soc. Industr. Mulhouse. Bulletin de la Société Industrielle de Mulhouse. Mulhouse.
Bull. Soc. Internat. Elec. Bulletin de la Société Internationale des Électriciens. Paris.
Bull. Soc. Naturalistes Moscou. Bulletin de la Société Imperiale des Naturalistes de Moscou. Moscow.
Bull. Soc. Path. Exot. Bulletin de la Société de Pathologie Exotique et de ses Filiales. Paris.
Bull. Soc. Philomath. Bulletin de la Société Philomathique. Paris.
Bull. Soc. Phys. Bulletin de la Société Francaise de Physique. Paris.
Bull. Soc Phys. Seances. Bulletin de la Société Francaise de Physique. Séances. Paris.
Bull. Soc. Roum. Phys. Bulletin de la Société Roumaine de Physique. Bucarest.
Bull. Soc. Roy. Sci. Liege. Bulletin de la Société Royale des Sciences de Liége. Liége.
Bull. Soc. Sci. Cluj. See *Bul. Soc. Stiinte Cluj.*
Bull. Soc. Vaud. Sci. Nat. Bulletin de la Société Vaudoise des Sciences Naturelles. Lausanne.
Bull. Tokyo Univ. Eng. Tokyo Imperial University. Faculty of Engineering. Bulletin. Tokyo.
Bull. Trav. Soc. Pharm. Bordeaux. Bulletin des Travaux de la Société de Pharmacie de Bordeaux. Bordeaux.
Bull. Univ. Illinois Eng. Expt. Station. Bulletin of the University of Illinois Engineering Experimental Station. Urnana, Ill.
Bull. U.S. Geol. Survey. Bulletins of the United States Geological Survey Department of the Interior. Washington.
Bull. Volcanol. Bulletin Volcanologique. Naples.
Bull. Waseda Col. Eng. Bulletin of Waseda College of Engineering. Japan.
Bur. Mines Bull. Bureau of Mines Bulletin Washington.
Bur. Mines Rep. Invest. Bureau of Mines Reports of Investigations. Washington.
Bur. Mines Tech. Paper. Bureau of Mines Technical Papers. Washington.
Bur. Stand. Bull Bulletin of the Bureau of Standards. Washington.
Bur. Stand. Circ. Bureau of Standards Circulars. Washington.
Bur. Stand. J. Res. Journal of Research of the National Bureau of Standards. Washington.
Bur. Stand. Misc. Publ. Bureau of Standards Miscellaneous Publications. Washington.
Byull. Eksptl. Biol. Med. Byulleten Eksperimental'noi Biologii i Meditsiny. Moscow.
Byull. Inst. Galurgii. Byulleten Instituta Galurgii.
Byull. IVNITI. Byulleten IVNITI.
Byull. Nauch.-Issledovatel. Khim. Farm. Inst. Byulleten Nauchno-Issledovatel'skogo Khimiko-Formatsevticheskogo Instituta.
Caliche.

Calif. J. Mines Geol. California Journal of Mines and Geology. San Francisco.

Cambr. and Dublin Math. J. Cambridge and Dublin Mathematical Journal. Cambridge.

Cambr. Math. J. Cambridge Mathematical Journal. Cambridge.

Canad. Chem. J. Canadian Chemical Journal. Toronto.

Canad. Chem. Met. Canadian Chemistry and Metallurgy. Toronto.

Canad. Chem. Process Ind. Canadian Chemistry and Process Industries. Toronto.

Canad. J. Chem. Canadian Journal of Chemistry. Ottawa.

Canad. J. Res. Canadian Journal of Research. Several Sections (A, B etc.). Ottawa.

Canad. J. Tech. Canadian Journal of Technology. Ottawa.

Canad. Med. Assoc. J. Canadian Medical Association Journal. Montreal.

Canad. Min. J. Canadian Mining Journal. Gardenvale, Quebec.

Cancer Res. Cancer Research. Chicago, London.

Canner. Chicago.

Caoutchouc and Rubber U.S.S.R. Moscow.

Carnegie Inst. Publ. Carnegie Institution of Washington. Publications. Washington.

Casopis Ceskoslov. Lekarnictva. Casopis Ceskoslovenskeho Lekarnictva. Prague.

Centr. Min. Centralblatt für Mineralogie, Geologie und Paläontologie. Sect. A (Mineralogie und Petrographie). Sect. B (Geologie und Paläontologie). Stuttgart. [Section A quoted unless otherwise state

Centr. Zuckerind. Centralblatt für die Zuckerindustri Magdeburg.

Ceram. Age. Ceramic Age. Newark, N.J.

Céram. et Verrerie. Çéramique et Verrerie.

Ceram. Ind. Ceramic Industry. Chicago.

Céramique. La Céramique. Paris.

Cereal Chem. Cereal Chemistry. Lancaster, Pa.

Chaleur et Ind. Chaleur et Industrie. Paris.

Chem. Age. Chemical Age. London.

Chem. Anal. Chemist Analyst. Phillipsburg, N.J.

Chem. App. Chemische Apparatur. Leipzig.

Chem. and Ind. Chemistry and Industry. London.

Chem. Ber. See *Ber.*

Chem. Centr. Chemisches Centralblatt. Berlin.

Chem. Corps J. Chemical Corps Journal. Washington.

Chem. Eng. Chemical Engineering. New York.

Chem. Eng. Mining Rev. Chemical Engineering and Mining Review. Sydney.

Chem. Eng. News. Chemical Engineering News. (American Chemical Society).

Chem. Eng. Prog. Chemical Engineering Progress. New York.

Chem. Erdr. Chemie der Erde. Jena, Germany.

Chem. Fabr. Die chemische Fabrik. Berlin. [Formerly Part B of Zeitschrift des vereins deutscher Chemie].

Chem. Gazette. Chemical Gazette. London.

Chem. Ing. Techn. See *Chemie Ingenieur Technik.*

Chem. Listy. Chemické Listy pro vědu a Průmysl. Prague.

Chem. Met. Eng. Chemical and Metallurgical Engineering. New York.

Chem. News. Chemical News. London.

Chem. Obzor. Chemický Obzor. Prague.

Chem. Prod. Chemical Products and the Chemical News. London.

Chem. Rev. Chemical Reviews. Baltimore.

Chem. Techn Die Chemische Technik. Berlin.

Chem. Trade J. Chemical Trade Journal and Chemical Engineer. London.

Chem. Weekbl. Chemisch Weekblad. Amsterdam.

Chem. Zentr. See *Chem. Centr.*

Chem. Ztg. Chemiker-Zeitung. Cöthen.

Chem. Zvesti. Chemické Zvesti. Bratislava, Czechoslovakia.

Chemie der Erde. Chemie der Erde. Beiträge zur chemischen Mineralogie, Petrographie und Geologie. Jena.

Chemie Ingenieur Technik. See *Z. Verein D. Ing. Beih. Verfahrungstechn.*

Chemist-Analyst. The Chemist-Analyst. Phillipsburg, N.J.

Chemist & Druggist. The Chemist and Druggist. London.

Chim. Anal. Chimie Analytique. Paris.

Chim. e Ind. La Chimica e l'Industria. Milan.

Chim. et Ind. Chimie et Industrie. Paris.

Chimcia (Brazil). Chimcia. São Paulo.

Chimica. Milan.

Chinese Chem. J. See *J. Chinese Chem. Soc.*

Chinese J. Phys. Chinese Journal of Physics. Shanghai.

Chinese J. Physiol. Chinese Journal of Physiology. Peking.

Chlor. Fako Rep.

Chymia. Chymia. Annual in the History of Chemistry. Philadelphia.

Civilingenieur. Der Civilingenieur. Leipzig.

Cleveland Clin. Quart. Cleveland Clinic Quarterly. Cleveland.

Clin. Sci. Clinical Science Incorporating Heart. London.

Coke and Chem. U.S.S.R. Koks i Khimiya. Kharkov.

Coll. Czech. Chem. Comm. Collection of Czechoslovak Chemical Communications. Prague.

Coll. Guardian. The Colliery Guardian and Journal of the Iron and Coal Trades. London.

Coll. J. U.S.S.R. Kolloid Zhurnal (Journal of Theoretical and Applied Colloid Chemistry and Physics). Moscow.

Coll. Rep. See *B.A. Rep. Coll. Chem.*

Coll. Res. Nat. Phys. Lab. Collected Researches. National Physical Laboratory. London.

Coll. Sympos. Ann. Colloid Symposium Annual. New York.

Colloques Internationaux du Centre National de la Recherche Scientifique. Paris.

Comm. Kodak Res. Lab. Communications of the Kodak Research Laboratory. Rochester, New York.

Comm. Leiden. Communications from the Physical [Kamerlingh Onnes] Laboratory of the University of Leiden. Leiden.

Comment. Phys. Math. Soc. Sci. Fenn. Societas Scientiarum Fennica Commentationes Physica-Mathematicae. Helsinki.

Comment. Soc. Reg. Sci. Gottingen. Commentationes Societatis Regiae Scientiarum Gottingensis, 1778–1808, ibid., Recentiores, 1808–41, Göttingen.

Compt. Rend. Comptes Rendus hebdomadaires des Séances de l'Académie des Sciences. Paris.

Compt. Rend. Acad. Agr. (Fran.). Comptes Rendus hebdomadaires des Séances de l'Académie d'Agriculture de France. Paris.

Compt. Rend. Acad. Sci. Roum. Comptes Rendus des Séances de l'Académie des Séances de Roumanie.

Compt. Rend. Soc. Biol. Comptes Rendus des Séances de la Société de Biologique. Paris.

Compt. Rend. Trav. Faculte Sci. Marseille. Comptes Rendus des Travaux de la Faculté des Sciences de Marseille. Marseille.

Compt. Rend. U.R.S.S. Comptes Rendus de l'Académie des Sciences de l'U.R.S.S. [See *Doklady*].

Confer. Viscos. Acad. Sci. U.S.S.R. Conference on Viscosity of Liquids and Colloidal Solutions. Academy of Sciences U.S.S.R. Moscow.

Conf. Lab. de Friedel. Conferences de Chimie faites au Laboratoire de M. Friedel. Four vols., Paris, 1888–94.

Congrès Internat. Élec. Procès-Verbaux Congrès Internationaux. Paris, 1900–2.

Congrès Internat. Phys. Congrès International de Physique. Paris, 1900–2.

Congrès Internat. du Froid. Congrès International du Froid. Paris.

Conn. Health Bull. Connecticut Health Bulletin.

Conseil Solvay. Institut Internationale de Chimie Solvay. Conseil de Chimie. Rapport et Discussions. Paris.

Cont. Met. Chem. Eng. Continental Metallurgical and Chemical Engineering.

Contrib. Estud. Cienc. Contribución al Estudio de las Ciencias Fisicas y Matemáticas. Universidad Nacional de La Plata. La Plata, Argentina.

Corrosion. Houston, Tex.

Cosmos. Paris.

Crell's Annalen. Chemische Annalen. Helmstädt. [Each annual volume is divided into two parts, i and ii].

Crown. The Crown. Baltimore.

Current Sci. Current Science. Bangalore.

Dansk. Vid. Math. Phys. Med. Kongelige Danske Videnskabernes Selskab, Matematisk-Fysiske Meddelelser. Copenhagen.

Dansk. Videns. Selsk. Det Kongelige Danske Videnskabernes Selskab. Forhandlinger. Copenhagen.

Das Papier. Darmstadt, Ger.

Debreceni Szemle. Debrecen, Hung.

Deut. Apothek. Ztg. Deutsche Apotheker Zeitung. Berlin.

Deut. Heilpflan. Deutsche Heilpflan.

Deut. Wollen-Gewerbe. Deutsche Wollen-Gewerbe.

Die Chemie. Berlin.

Die Technik. Berlin.

Die Wärme. Berlin.

Die Wissenschaft. Brunswick.

Dingl. J. Dingler's Polytechnisches Journal. Berlin.

Discuss. Faraday Soc. Discussion. Faraday Society. London.

Dissert. Dissertation.

Doklady. Doklady Akademii Nauk U.S.S.R. Moscow.

Doklady Vses. Doklady Vsesoyuznoi Akademii Sel'sko-Khozyaistvennykh Nauk imeni V.I. Lenina.

Dopovidi Akad. Nauk U.R.S.R. Dopovidi Akademii Nauk Ukrains'koi R.S.R. Kiev, U.R.S.R.

D.S.I.R. Food Invest. Board Rep. Department of Scientific and Industrial Research. Report of the Food Investigation Board. London.

D.S.I.R. Fuel Res. Paper. Department of Scientific and Industrial Research. Water Pollution Research. Summary of Current Literature. London.

Eclair. Élec. Éclairage Électrique. Paris.

Econo. Geol. Economic Geology. Lancaster, Pa.

Edin. J. Sci. Edinburgh Journal of Science. Edinburgh.

Edin. Med. J. Edinburgh Medical Journal. Edinburgh.

Edin. N. Phil. J. Edinburgh New Philosophical Journal. Edinburgh.

Edin. Phil. J. Edinburgh Philosophical Journal. Edinburgh.

Elec. Comm. Electrical Communication. New York.

Elec. News, (Toronto). Electrical News, Toronto.

Elec. Rev. Electrical Review. London.

Elec. Rev. (Chicago). Electrical Review. Chicago.

Elec. World. Electrical World. New York.

Electrician. The Electrician. London.

Electrochem. Met. Ind. Electrochemical and Metallurgical Industry. New York.

Elektrochem. Z. Elektrochemische Zeitschrift. Berlin.

Electronics. New York.

Electrotech. J. Japan. Electrotechnical Journal (Japan). Tokyo. (Now Deuki Gakkai Zasshi).

Elektrotech. Z. Elektrotechnische Zeitschrift. Berlin.

Elster-Geitel Festschr. Arbeiten aus den Gebieten der Physik, Mathematik, Chemie. Festschrift Julius Elster und Hans Geitel. Brunswick, 1915.

Emailwaren Ind. Emailwaren-Industrie. Duisburg.

Ency. Brit. Encyclopædia Britannica.

Endeavour. London.

Endocrinolog. Endocrinology. Oxford.

Energia Termica. Milan.

Eng. Boiler House Review. Engineering and Boiler House Review. Maidenhead, Berks.

Eng. Contract Record. Engineering and Contract Record. Toronto.

Eng. J. Canada. The Engineering Journal. Engineering Institute of Canada. Montreal.

Eng. Mining. J. Engineering and Mining Journal. New York.

Eng. News. Engineering News. A Journal of Civil, Mechanical, Mining and Electrical Engineering. New York.

Engineer. The Engineer. London.

Engineering. London.

Entomol. Soc. Ontario Ann. Rep. Entomological Society of Ontario, Annual Report.

Enzykl. d. Math. Wiss. Enzyklopädie der mathematischen Wissenschaften. Leipzig.

Enzymologia. The Hague, Netherlands.

Erdöl u. Köhle. Erdöl und Köhle. Berlin.

Ergebn. exakt. Naturwiss. Ergebnisse der exakten Naturwissenschaften. Berlin.

Ergebn. Inn. Med. Kind. Ergebnisse der inneren Medizin und Kinderheilkunde. Berlin-Charlottenburg.

Ergebn. Physiol. Ergebnisse der Physiologie. Munich.

Essays and Obs. Phys. and Lit. Essays and Observations Physical and Literary. Edinburgh.

Estudos Notas e Trabalho. Serv. Fomento Min. (Portugal). Estudos, Notas e Trabalhos do Servico de Fomento Mineiro (Portugal).

Experientia. Basel.

Farbe u. Lack. Farbe und Lack. Hanover.

Farm. Zhur. Farmatsevticheskii Zhurnal. Kiev, Ukraine.

Farmatsiya. Moscow.

Farmatsiya i Farmakol. Farmatsiya i Farmakologiya. Moscow.

Farm. Moderna. Farmacia Moderna.

Federal Register. Washington.

Ferrum. Halle.

Fertigungstech. Fertigungstechnik. Munich.

Fettchem. Umschau. Fettchemische Umschau. Stuttgart.

Fette u. Seifen. Fette und Seifen. Münster.

FIAT Rev. German Sci. FIAT Review of German Science. Office of Military Government for Germany. Field Information Agencies Technical. Wiesbaden.

Finska Kem. Medd. Finska Kemistsamfundets Meddelanden. Helsinki.

Foldtani Közlöny. Budapest.

Folia Endocrin. Japon. Folia Endocrinologica Japonica. Tokyo.

Food Inds. Food Industries. New York.
Food. Invest. Board Rep. See *D.S.I.R. Food Invest. Board Rep.*
Foreign Petrol. Techn. Foreign Petroleum Technology. Linden, New Jersey.
Forhl. Vidensk.-Selsk. Christiana. Forhandlinger i Videnskabs-Selskabet i Christiana. Christiana.
Forsch. auf d. Gebiete Agrikult. Phys. Forschungen auf dem Gebiete der Agrikultur-Physik. Heidelberg.
Forschungen u. Fortschritte. Forschungen und Fortschritte. Berlin.
Forschungsarb. Gebiet Ingenieurwes. Mitteilungen uber Forschungsarbeiten aus dem Gebiet des Ingenieurwesens. Berlin.
Fortschr. Chem. Phys. phys. Chem. Fortschritte der Chemie, physik und physikalische Chemie. Berlin.
Fortschr. Landw. Fortschritte der Landwirtschaft.
Fortschr. Min. Krist. Petr. Fortschritte der Mineralogie, Kristallographie und Petrographie. Jena.
Fortschr. Phys. Fortschritte der Physik. Berlin, 1846–1919.
Foundry. Cleveland, Ohio.
Foundry Trade J. Foundry Trade Journal. London.
Frankfurt. Z. Path. Frankfurter Zeitschrift für Pathologie. Munich.
Frontier. The Frontier. Chicago, Mexico.
Fuel. Fuel in Science and Practice. London.
Fysisk Tidsskr. Fysisk Tidsskrift. Copenhagen.
G.E.C. Journ. G.E.C. Journal. General Electric Co. London.
Gac. Méd. Mex. Gaceta Médica de Mexico. Mexico.
Gas Age. New York.
Gas Age-Record. New York.
Gas-Ind. Die Gas-Industrie. Halle.
Gas J. Gas Journal. London.
Gas Research Board Comm. Gas Research Board Communication. London.
Gas u. Wasserfach. Das Gas- und Wasserfach. Munich and Berlin.
Gas World. London.
Gazz. Gazzetta Chimica Italiana. Rome.
Gen. Elec. Rev. General Electric Review. Schenectady, N.Y.
Génie Civile. Le Génie Civile. Paris.
Geographical Rev. Geographical Review.
Geol. Fören. Stockholm Forh. Geologiska Föreningens i Stockholm Förhandlingar. Stockholm.
Geol. Surv. G. Britain, Summ. Prog. Geological Survey of Great Britain, Summary of Progress. London.
Geophys. Lab. Carnegie Inst. Paper. Papers from the Geophysical Laboratory. Carnegie Institute. Washington.
Ges. Abhl. Gesammte Abhandlungen.
Ges. Werke. Gesammelte Werke.
Gesundh. Ing. Gesundheits-Ingenieur. Munich.
Gesundheit u. Wohlfahrt. Gesundheit und Wohlfahrt.
Giesserei. Munich.
Giesserie Ztg. Giesserei Zeitung. Berlin.
Gigiena i Sanit. Gigiena i Sanitariya. Moscow.
Giorn. Chim. Ind. Appl. Giornale di Chimica Industriale ed Applicata. Milan.
Glas u. App. Glas und Apparat. Weimar.
Glashütte. Die Glashütte. Dresden.
Glass. Northwood, Middlesex.
Glastech. Ber. Glastechnische Bericht. Frankfort.
Gött. Nachr. Nachrichten der Akademie der Wissenschaften zu Göttingen. Mathematisch-Physikalischer Klasse. Berlin.
Guy's Hosp. Gaz. Guy's Hospital Gazette. London.

Hahnemannian Monthly. West Pittston, Pa.
Hawaii Agr. Expt. Sta., Ann. Rept. Hawaii Agricultural Experimental Station, Annual Report. Honolulu.
Heating, Piping, Air Conditioning. Chicago.
Heidelberg Ber. Sitzungsberichte der Heidelberger Akademie der Wissenschaften. Mathematisch-Naturwissenschaftliche Klasse. Heidelberg.
Helv. Chim. Acta. Helvetica Chimica Acta. Basel.
Helv. Phys. Acta. Helvetica Physica Acta. Basel.
Higuèna Truda. Basel.
Hilgardia. Berkeley, California.
Hist. Acad. Berlin. Histoire de l'Académie Royale des Sciences et des Belles Lettres de Berlin. Berlin.
Hist. Acad. Sci. (Paris). See *Mém. Acad. Sci.*
Holzmarkt Berl. Berliner Holzmarkt.
Hungar. Acta Phys. Hungarica Acta Physica. Budapest.
Hydrochem. Mat. U.S.S.R. Hydrochemische Materialien U.S.S.R.
Ice and Cold Storage. London.
Ice and Refrig. Ice and Refrigeration. Chicago.
Illum. Eng. Illuminating Engineer. London.
Ind. Chem. Industrial Chemist and Chemical Manufacturer. London.
Ind. Chim. Belg. L'Industrie Chimique Belge. Brussels.
Ind. Eng. Chem. Industrial and Engineering Chemistry. Easton, Pa.
Ind. Eng. Chem. Anal. Industrial and Engineering Chemistry. Analytical. Easton, Pa.
Ind. Gas. Industrial Gas. Philadelphia.
Ind. Heating. Industrial Heating. Pittsburg, Pa.
Ind. Med. Industrial Medicine. Chicago.
Ind. Plastics. Industrial Plastics. Cleveland, Ohio.
Ind. Plastique. Industries des Plastiques. Paris.
Ind. y Quim. Industria y Quimica. Buenos Aires.
India Rubber World. New York.
Indian Forest Records. Dehra Dun.
Indian J. Agric. Sci. Indian Journal of Agricultural Science. Delhi.
Indian J. Phys. Indian Journal of Physics. Calcutta.
Indian Lac Res. Inst. Ann. Rep. Indian Lac Research Institute. Reports. Ranchi, Bihar.
Indian Med. J. Indian Medical Journal.
Indian Textile J. Indian Textile Journal. Bombay.
Industria Chimica. L'Industria Chimica. Milan.
Industrie Chim. Industrie Chimique. Paris.
Inform. Quim. Información de Quimica Analitica. Madrid.
Ingenieur. Die Ingenieur. The Hague, Holland.
Ingenieur Arch. Ingenieur-Archiv. Berlin.
Ingenieur Chim. L'Ingenieur Chimiste. Brussels.
Inorg. Synth. Inorganic Syntheses. New York.
Inst. Forestal. Instituto Forestal de Investigaciones y Experiencias (Madrid), Boletin.
Inst. Min. Met. London. Institution of Mining and Metallurgy. London.
Instruments. Pittsburg, Pa.
Int. Congr. Testing Mat. International Congress for Testing Materials. Association Internationale pour l'Essai des Materiaux. Zurich, 1931, 2 vols.
Int. Congr. Angew. Chem. Kongress für angewandte Chemie. Berlin, 1903.
Intern. Rev. Ges. Hydrobiol. Internationale Revue der gesamten Hydrobiologie und Hydrographie. Leipzig.
Intern. Sugar J. International Sugar Journal. London.
Internat. Conf. Phys. International Conference on Physics. The Physical Society. London, 1935.

Internat. Congr. Refrig. Proceedings of the International Congress of Refrigeration. The Hague, Holland.

Internat. Crit. Tables. International Critical Tables. New York, London.

Internat. Z. Metallogr. Internationale Zeitschrift für Metallographie. Berlin.

Ion. Madrid.

Iowa State Coll. J. Sci. Iowa State College Journal of Science. Ames, Iowa.

Iron Age. New York.

Iron and Steel. London.

Iron and Steel Inst. Rep. Iron and Steel Institute. Special Report. London.

Iron and Steel Mag. Iron and Steel Magazine. Boston.

Iron Coal Trades Review. The Iron and Coal Trades Review. London.

Iron Steel Inst. Carnegie Mem. Carnegie Scholarship Memoirs. Iron and Steel Institute. London.

Isis. Ghent.

Issy. Zjazd. Chem. Polsk.

Isvest. Fis. Nauk. Isvestiya Seriyá Fisicheskaya. Moscow.

Izvest. Akad. Nauk S.S.S.R. Izvestiya Akademii Nauk Soyuza Sovetskikh Sotsialisticheskikh Respublik.

Izvest. Nov. Izvestiya Noveĭsheĭ Sel'sko-Khozyaĭstvennoĭ Tekhnekí.

J.A.C.S. Journal of the American Chemical Society. Easton, Pa.

J.A.M.A. Journal of the American Medical Association. Chicago, London.

J. Acoust. Soc. Amer. Journal of the Acoustical Society of America. Lancaster, Pa.

J. Agr. Chem. Soc. Japan. Journal of the Agricultural Chemical Society of Japan. Tokyo.

J. Agr. Prat. Journal d'Agriculture Pratique et Journal de l'Agriculture.

J. Agr. Res. Journal of Agricultural Research. Washington.

J. Amer. Ceram. Soc. Journal of the American Ceramic Society. Easton, Pa.

J. Amer. Inst. Elec. Eng. Journal of the American Institute of Electrical Engineers. New York.

J. Amer. Leather Chem. Journal of the American Leather Chemists Association. Cincinnati, Ohio.

J. Amer. Med. Assoc. Journal of the American Medical Association. Chicago.

J. Amer. Oil Chemists' Soc. Journal of the American Oil Chemists' Society. Chicago.

J. Amer. Orient. Soc. Journal of the American Oriental Society. New York.

J. Amer. Pharm. Assoc. Journal of the American Pharmaceutical Association. Baltimore.

J. Amer. Rocket Soc. Journal of the American Rocket Society. New York.

J. Amer. Soc. Agron. Journal of the American Society of Agronomy. Geneva, N.Y.

J. Amer. Soc. Mech. Eng. Journal of the American Society of Mechanical Engineers. New York.

J. Amer. Soc. Refrig. Eng. Journal of the American Society of Refrigerating Engineers. New York.

J. Amer. Vet. Med. Assoc. Journal of the American Veterinary Medical Association. Chicago.

J. Amer. Waterwks. Assoc. Journal of the American Water Works Association. New York.

J. Animal Sci. Journal of Animal Science. Ithaca, N.Y.

J. Appl. Chem. Journal of Applied Chemistry. Society of Chemical Industry. London.

J. Appl. Chem. U.S.S.R. Journal of Applied Chemistry U.S.S.R.

J. Appl. Mechan. Journal of Applied Mechanics. Issued as part of the Transactions of the American Society of Mechanical Engineers. New York.

J. Appl. Phys. Journal of Applied Physics. Lancaster, Pa.
J. Appl. Phys. U.S.S.R. Journal of Applied Physics. Moscow.
J. Asiat. Journal Asiatique. Paris.
J. Assoc. Offic. Agr. Chem. Journal of the Association of Official Agricultural Chemists. Washington.
J. Australian Inst. Agr. Sci. Journal of the Australian Institute of Agricultural Science. Melbourne.
J. Bact. Journal of Bacteriology. Baltimore.
J. Biochem. (Japan). Journal of Biochemistry (Japan). Tokyo.
J. Biol. Chem. Journal of Biological Chemistry. Baltimore.
J. Cellular Comp. Physiol. Journal of Cellular and Comparative Physiology. Philadelphia, Pa.
J. Chem. Educ. Journal of Chemical Education. Easton, Pa.
J. Chem. Ind. Japan. Journal of Chemical Industry (Japan). Tokyo.
J. Chem. Ind. U.S.S.R. Journal of the Chemical Industry of the U.S.S.R. Moscow.
J. Chem. Phys. The Journal of Chemical Physics. American Institute of Physics. Lancaster, Pa.
J. Chem. Phys. (Gehlen). Journal für die Chemie, Physik und Mineralogie. 9 vols., Berlin, 1806-10.
J. Chem. Phys. (Schweigger). Journal für Chemie und Physik. Nürnberg.
J.C.S. Journal of the Chemical Society. London.
J. Chem. Soc. Japan. Journal of the Chemical Society of Japan. Tokyo.
J. Chem. Soc. Muslim Univ. Aligarh. Journal of the Muslim University Chemical Society. Aligarh.
J. Chim. Phys. Journal de Chimie Physique. Geneva, and (from 1906) Paris.
J. Chinese Chem. Soc. Journal of the Chinese Chemical Society. Peiping.
J. Coll. Sci. Imp. Univ. Japan. Journal of the College of Science. Imperial University of Tokyo. Tokyo.
J. Colloid Sci. Journal of Colloid Science. New York.
J. Colo.-Wyo. Acad. Sci. Journal of the Colorado/Wyoming Academy of Science.
J. Counc. Sci. Ind. Res. (Australia). Journal of the Council for Scientific and Industrial Research. Melbourne.
J. Dairy Res. Journal of Dairy Research. London.
J. Dairy Sci. Journal of Dairy Science. St. Leonards, Australia.
J. Dental Res. Journal of Dental Research. St. Lous, U.S.A.
J. de l'École Polytechn. Journal de l'École Polytechnique. Paris.
J. de Math. (Liouville). Journal des Mathématiques Pures et Appliquées. Paris.
J. de Phys. Journal de Physique Théorique et Appliqué. Paris.
J. de Phys. Old series: Journal de Physique, de Chimie, d'Histoire Naturelle et des Arts. Paris, 53 vols., 1794-1823.
J. der Pharmacie. Journal der Pharmacie. Leipzig (1794-1817).
J. der Phys. Journal der Physik. Halle and Leipzig.
J. Econ. Entomol. Journal of Economic Entomology. College Park, Md.
J. Electrochem. Assoc. Japan. Journal of the Electrochemical Association of Japan. Tokyo.
J. Electrochem. Soc. Journal of the Electrochemical Society. Baltimore, Md.
J. Electrodepos. Techn. Soc. Journal of the Electrodepositors' Technical Society. London.
J. Electropl. Depos. Techn. Soc. Journal of the Electroplaters' and Depositors' Technical Society. London.
J. Exptl. Med. Journal of Experimental Medicine. Baltimore, New York.
J. Exptl. Theor. Phys. U.S.S.R. Journal of Experimental and Theoretical Physics U.S.S.R. Moscow, Leningrad.

J. f. Math. (Crelle). See *J. Reine Angew. Math. (Crelle).*

J. Fac. Eng. Tokyo. Imperial University, Tokyo. Journal of the Faculty of Engineering. Tokyo.

J. Fac. Sci. Imp. Univ. Tokyo. Imperial University, Tokyo. Journal of the Faculty of Science. Tokyo.

J. Fisheries Board Can. Journal of the Fisheries Research Board of Canada. Toronto.

J. Franklin Inst. Journal of the Franklin Institute. Philadelphia.

J. Fuel Soc. Japan. Journal of the Fuel Society of Japan. Tokyo.

J. Gasbeleucht. Journal fur Gasbeleuchtung. Munich.

J. Gas Lighting. Journal of Gas Lighting and Water Supply. London.

J. Gen. Chem. U.S.S.R. Journal of General Chemistry U.S.S.R. Moscow.

J. Gen. Physiol. Journal of General Physiology. New York.

J. Geol. The Journal of Geology. Chicago.

J. Hotel-Dieu Montreal. Journal de l'Hotel-Dieu de Montreal. Montreal.

J. Hyg. Journal of Hygiene. London, New York.

J. Immunol. Journal of Immunology. Baltimore.

J. Imp. Coll. Chem. Eng. Soc. Journal of the Imperial College Chemical Engineering Society. London.

J. Ind. Eng. Chem. Journal of Industrial and Engineering Chemistry. Washington.

J. Ind. Hyg. Toxicol. Journal of Industrial Hygiene and Toxicology, with Abstract of the Literature. Baltimore.

J. Indian Chem. Soc. Journal of the Indian Chemical Society. Calcutta.

J. Indian Inst. Sci. Journal of the Indian Institute of Sciences. Mysore.

J. Infectious Diseases. Journal of Infectious Diseases. Chicago, London.

J. Inst. Chem. Journal of the Institute of Chemistry (now Journal of the Royal Institute of Chemistry). London.

J. Inst. Elec. Eng. Journal of the Institution of Electrical Engineers. London.

J. Inst. Fuel. Journal of the Institute of Fuel. London.

J. Inst. Heating and Ventilating Eng. Journal of the Institute of Heating and Ventilating Engineers. London.

J. Inst. Met. Journal of the Institute of Metals and Metallurgical Abstracts. London.

J. Inst. Petrol. Journal of the Institute of Petroleum. London.

J. Inst. Petrol. Techn. Journal of the Institution of Petroleum Technologists. London.

J. Inst. Sanit. Engrs. Journal of the Institution of Sanitary Engineers. London.

J. Inst. Water Engrs. Journal of the Institution of Water Engineers. London.

J. Internat. Soc. Leather Trades Chem. Journal of the International Society of Leather Trades' Chemists. London.

J. Iron Steel Inst. Journal of the Iron and Steel Institute. London.

J. Japan. Ceram. Assoc. Journal of the Japanese Ceramic Association. Tokyo.

J. Lab. Clin. Med. Journal of Laboratory and Clinical Medicine. St. Louis, Mo.

J. Marine Res. Journal of Marine Research. New Haven, Conn.

J. Math. See *J. de Math.*

J. Math. Phys. Mass. Inst. Journal of Mathematics and Physics. Massachusetts Institute of Technology. Cambridge, Mass.

J. Metals. Journal of Metals. New York.

J. Milk Trade Tech. Journal of Milk Trade Technology.

J. Mines. Journal des Mines. Paris.

J. Mysore Univ. The Half-Yearly Journal of the Mysore University. Bangalore.

J.N.Y. Entomol. Soc. Journal of the New York Entomological Society. New York.
J. New England Water Works Assoc. Journal of the New England Water Works Association. Boston, Mass.
J. Nutrition. Journal of Nutrition. Philadelphia, Pa.
J. Oil Colour Chem. Assoc. Journal of the Oil and Colour Chemists' Association. London.
J. Opt. Soc. Amer. Journal of the Optical Society of America. Lancaster.
J. Org. Chem. Journal of Organic Chemistry. Baltimore.
J. Oriental Med. Journal of Oriental Medicine (later Manshu Igaku Zasshi), Mukden.
J. Osmania Univ. Journal of the Osmania University. Deccan, India.
J. Penna. Water Works Operators' Assoc. Journal of the Pennsylvania Water Works Operators' Association. State College, Pa.
J. Pharm. Belg. Journal de Pharmacie de Belgique. Brussels.
J. Pharm. Chim. Journal de Pharmacie et de Chimie. Paris.
J. Pharmacol. Journal of Pharmacology. London.
J. Phys. Journal de Physique, Théorique et Appliquée.
J. Phys. Chem. The Journal of Physical Chemistry. Ithaca, N.Y., Baltimore.
J. Phys. Chem. U.S.S.R. Journal of Physical Chemistry U.S.S.R. Moscow.
J. Phys. Coll. Chem. Journal of Physical and Colloid Chemistry. Baltimore.
J. Phys. Radium. Journal de Physique, et le Radium. Paris.
J. Phys. Soc. Japan. Journal of the Physical Society of Japan. Tokyo.
J. Phys. U.S.S.R. Journal of Physics U.S.S.R. Moscow, New York.
J. Physiol. Journal of Physiology. London.
J. Physiol. Path. Gén. Journal de Physiologie et de Pathologie Générale. Paris.
J. Physiol. U.S.S.R. Journal of Physiology of U.S.S.R. Moscow, Leningrad.
J. Polymer Sci. Journal of Polymer Science. New York.
J. Prakt. Chem. Journal für praktische Chemie. Leipzig.
J. Proc. Asiatic Soc. Bengal. Journal of the Proceedings of the Asiatic Society of Bengal. Bengal.
J. Proc. Austral. Chem. Inst. Journal and Proceedings of the Australian Chemical Institute. Melbourne.
J. Proc. Roy. Soc. N.S. Wales. Journal and Proceedings of the Royal Society of New South Wales. Sydney.
J. Rational Mech. Anal. The Journal of Rational Mechanics and Analysis. Bloomington, Indiana.
J. Reine Angew. Math. (Crelle). Journal für die reine und angewandte Mathematik (Crelle's Journal). Berlin.
J. Res. Nat. Bur. Stand. Journal of Research of the National Bureau of Standards. Washington.
J. Rheol. Journal of Rheology. Easton, Pa.
J. Roy. Army Med. Corps. Journal of the Royal Army Medical Corps. London.
J. Roy. Astron. Soc. Canada. Journal of the Royal Astronomical Society of Canada. Richmond Hills, Ontario.
J. Roy. Inst. Journal of the Royal Institution of Great Britain. London.
J. Roy. Inst. Chem. Journal of the Royal Institute of Chemistry. London.
J. Roy. Soc. Arts. Journal of the Royal Society of Arts. London.
J. Roy. Soc. N.S. Wales. Journal of the Royal Society of New South Wales. Sydney.
J. Roy. Techn. Coll. Glasgow. Journal of the Royal Technical College. Glasgow.
J. Rubber Res. Journal of Rubber Research. London.
J. Russ. Phys. Chem. Soc. Journal of the Russian Physical-Chemical Society. Moscow. (C = Chemistry section, P = Physics Section).

J.S.C.I. Journal of the Society of Chemical Industry. London.

J. S.-E. Agr. Coll. Wye. Journal of the Southeastern Agricultural College, Wye, Kent.

J. Sci. Assoc. Maharajah's College, Vizianagaram. Journal of the Science Association, Maharajah's College, Vizianagaram.

J. Sci. Hiroshima Univ. Journal of Science of the Hiroshima University. Hiroshima, Japan.

J. Sci. Ind. Res. India. Journal of Scientific and Industrial Research. National Physical Laboratory. New Delhi, India.

J. Sci. Instr. Journal of Scientific Instruments and of Physics in Industry. London.

J. Sci. Res. Tokyo. Journal of Scientific Research. Tokyo.

J. Soc. Arts. See *J. Roy. Soc. Arts.*

J. Soc. Chem. Ind. Japan. Journal of the Society of Chemical Industry. Tokyo.

J. Soc. Cosmetic Chem. Journal of the Society of Cosmetic Chemists. Grosse Point Farms, Mich.

J. Soc. Dyers Colourists. Journal of the Society of Dyers and Colourists. Bradford.

J. Soc. Glass Technol. Journal of the Society of Glass Technology. Sheffield.

J. Soc. Leather Trades Chem. Journal of the Society of Leather Trades Chemists (now Journal of the International Society of Leather Trades Chemists). Croydon.

J.S. African Chem. Inst. Journal of the South African Chemical Institute. Cape Town.

J. Tech. Phys. U.S.S.R. Journal of Technical Physics U.S.S.R. Leningrad.

J. Text. Inst. Journal of the Textile Institute. Manchester.

J. Tokyo Chem. Soc. Journal of the Tokyo Chemical Society. Tokyo.

J. Trop. Med. Hyg. Journal of Tropical Medicine and Hygiene. London, New York.

J. Univ. Bombay. Journal of the University of Bombay. Bombay.

J. Usines Gaz. Journal des Usines à Gaz. Paris.

J. Wash. Acad. Journal of the Washington Academy of Sciences. Washington.

J. Western Soc. Eng. Journal of the Western Society of Engineers. Oak Park, Ill.

Jahrb. f. Berg- u. Hütten-Wesen in Sachsen. Jahrbuch für Berg- und Hütten-Wesen in Sachsen. Freiberg.

Jahrb. Geol. Reichsanst. Wien. Jahrbuch der Kaiserlich-Königlichen Geologischen Reichsanstalt. Vienna.

Jahrb. Hamburg. Wiss. Anst. Jahrbuch der Hamburgischen wissenschaften Anstalten. Hamburg.

Jahrb. Min. Jahrbuch für Mineralogie, Geognosie, Geologie und Petrifaktenkunde. Heidelberg, 3 vols., 1830–2.

Jahrb. Niedersächs. Geol. Verein. Jahresbericht der Niedersächsischen Geologischen Vereins. Hanover.

Jahrb. Radioakt. Elektronik. Jahrbuch der Radioaktivität und Elektronik. Leipzig.

Jahresb. Jahresbericht über die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften. Giessen und Brunswick.

Jahres-Ber. Jahres-Bericht über die Fortschritte der Chemie und Mineralogie. Tübingen.

Jahresber. Chem. Tech. Reichsanstalt. Jahresbericht für Chemische-Technologische Reichsanstalt.

Japan. J. Phys. Japanese Journal of Physics. Tokyo.

Jern-Kontorets Annaler. Stockholm.

K. Dansk. Videns. Selsk. Meddel. Det Kongelige Danske Videnskabernes Selskab Matematisk-Fysiske Meddelelsen. Copenhagen.

K. Norsk. Vidensk. Selsk. Forhl. Kongelige Norske Videnskabernes Selskabs Forhandlinger. Trondheim.

K. Svensk. Akad. Handl. Kongliga Svenska Vetenskaps-Akademiens Handlinger. Uppsala and Stockholm.

Kagaku no Ryoîki. Tokyo.

Kali. Berlin.

Kaliǐ U.S.S.R. Moscow.

Kalteind. Kalteindustrie. Hamburg and Altona.

Kastners, Archiv. Archiv für die gesammte Naturlehre. Nürnberg, 18 vols., 1824–9.

Kautschuk. Berlin and Düsseldorf.

Kém. Lapja. Kémikusok Lapja. Budapest.

Keramos. Bamberg.

Kgl. Dansk. Videns. Det Kongelige Danske Videnskabernes Selskabs. Skrifter. Naturvidenskabelige og Mathematiske Afdeling. Copenhagen.

Kgl. Norske Videns. Kongelige Norske Videnskabers Selskabs, Forhandlinger. Trondheim.

Khim. Farm. Prom. Khimiko-Farmatsevticheskaya Promyshlennost.

Khim. Mashinostroenie. Khimicheskoe Mashinostroenie.

Khim. Prom. Khimicheskaya Promyshlennost. Moscow.

Khimstroǐ. Moscow.

Klassiker. See Ostwald.

Klein. Veröffentl. Kgl. Ungar. Reichsanst. Meteor. Erdmagnet. Kleinere Veröffentlichungen der dem Kgl. Ungar. Ministerium fur Ackerbau unterstehenden Kgl. Ungar. Reichsanstalt für Meteorologie und Erdmagnetismus. Budapest.

Kleine Mitl. Ver. Wasser. Boden. Lufthyg. Kleine Mitteilungen für die Mitgleider des Vereins für Wasser-, Boden- und Lufthygiene. Berlin-Dahlem.

Klin. Med. U.S.S.R. Klinicheskaya Meditsina (U.S.S.R.). Moscow.

Klin. Wochschr. Klinische Wochenschrift. Berlin, London.

Koll. Beih. Kolloidchemische Beihefte. Dresden.

Koll. Z. Kolloid Zeitschrift. Dresden and Frankfurt.

Korroziya i Borba. Korroziya i Borba s Neǐ.

Kosmos. Lwow.

Kranke Pflanze. Dresden.

Lab. Allgem. Phys. Tech. Chem. (Univ. Fernen Österr.). Laboratorium für Allgemeine Physikalische und Technische Chemie (University Fernen Osterreiche).

Lancet. London.

Landw. Jahrb. Landwirtschaftliche Jahrbücher. Berlin.

Landw. Vers. Sta. Landwirtschaftlichen Versuchs-Stationen.

Landolt-Börnstein 'Tabellen'. Landolt-Börnstein, Physikalisch-Chemische Tabellen, and Ergänzungsbände. Berlin.

La Nature. Paris.

Le Radium. Paris.

Le Vide. Paris.

Legkie Metal. Legkie Metally (Light Metals). Moscow.

Leipzig Ber. Berichte über die Vorhandlungen der Königlich Sächsischen Akademie der Wissenschaften zu Leipzig. Mathematisch-Physikalische Klasse. Leipzig.

Leipzig. Monat. Text. Ind. Leipziger Monatsschrift für Textil-Industrie. Leipzig.

Lékárnictva.

Licht u. Lampe. Licht und Lampe. Berlin.

Light Metal Age. Chicago.

L'Industrie Chim. L'Industrie Chimique. Paris.

Lingnan Sci. J. Lingnan Science Journal. Lingnan University. Canton, China.

L'Institut. Paris.
Listy Cukrovar. Listy Cukrovarniké. Prague.
Litaĭnoe Delo.
Lnopenkodsnutovaya Prom. Lnopenkodsnutovaya Promyshlennost.
Lunds Fys. Sällsk. Jubelskrift. Kungl. Fysiografiska Sällskapets i Lund. Jubelskrift. Lund, 1878.
Lychnos. Uppsala.
Mag. Kém. Lapja. Magyar Kémikusok Lapja. Budapest.
Magyar Chem. Fol. Magyar Chemiai Folyóirat. Budapest.
Magyar Gyógy. Társa. Értes. Magyar Gyógyszerésztudományi Társaság Értesitõje. Budapest.
Magyar Orvosi Arch. Magyar Orvosi Archivum. Budapest.
Manch. Mem. Memoirs and Proceedings of the Manchester Literary and Philosophical Society. Manchester.
Marburg Ber. Sitzungsberichte der Gesellschaft zur Beförderung der gesamten Naturwissenschaften zu Marburg. Marburg.
Materialy Nauch. Issle. Materialy Tsentral'nogo Nauchno-Issledovatel'skogo Instituta po Tekstil'noĭ Promyshlennosti 'Niti'.
Math. Ann. Mathematische Annalen. Leipzig.
Math. Anz. Ungar. Akad. Wiss. Matematikai és Természettudomanyi Értesitó a Magyar Tudományos Akademia. Budapest.
Math. Nat. Ber. Ungarn. Mathematische und Naturwissenschaftliche Berichte aus Ungarn. Leipzig.
Math. Z. Mathematische Zeitschrift. Brunswick.
Mech. Eng. N.Y. Mechanical Engineering. New York.
Mechanics Magazine. London (1823–72).
Medd. Stat. Vaxtskyddum. Meddelanden från Statens Växtskyddum.
Meddel. Nobelinst. Meddelanden från K. Svenska Vetenskapsakademiens Nobelinstitut. Uppsala.
Medel. Vlaam. Chem. Ber. Mededelingen van de Vlaamse Chemische Vereniging. Ghent, Belg.
Melliand Textilber. Melliand Textilberichte. Heidelberg.
Mém. Acad. Berlin. Mémoires de l'Académie Royale des Sciences et Belles-Lettres. Berlin (1786–1804).
Mem. Acad. Ciencias Arts Barcelona. Memòires de l'Acadèmia de Ciències i Arts de Barcelona. Barcelona.
Mém. Acad. Roy. Belg. Académie Royale de Belgique. Mémoires. Classe des Sciences. Collection in 8vo. Brussels.
Mém. Acad. Sci. Mémoires de l'Académie des Sciences. Paris. Abstracts of the memoirs are added to many of the volumes with the title Histoire.
Mém. Acad. St. Petersb. Mémoires de l'Académie Imperiale des Sciences de St. Petersbourg. St. Petersburg.
Mém. Acad. Turin. Mémoires de l'Académie Royale des Sciences à Turin. Turin.
Mem. Accad. Ital. Chim. Memorie della Accademia della Italiana Chimica.
Mem. Accad. Lincei. Memorie della Reale Accademie Nazionale dei Lincei. Classe di Scienze Fisischa. Rome.
Mem. R. Accad. Torino. Memorie della Reale Accademia de Scienza di Torino. Turin.
Mem. Chem. Soc. Memoirs of the Chemical Society. London.
Mem. Coll. Eng. Kyushu Imp. Univ. Memoirs of the College of Engineering. Kyushu. Imperial University. Fukuoka, Japan.
Mem. Coll. Sci. Kyoto Imp. Univ. Memoirs of the College of Science. Kyoto Imperial University. Kyoto.
Mém. Couronn. et Autres Acad. Roy. Belg. Mémoires Couronnés et Autres Mémoires Publiés par l'Académie Royale des Sciences, des Lettres et des Beaux-Arts de Belgique. 8vo, Brussels.

Mém. Couronn. Acad. Roy. Belg. Mémoires Couronnés par l'Académie Royale des Sciences et Belles-Lettres de Bruxelles. 4 to. Brussels.

Mém. Couronn. et de Sav. Étrang. Acad. Roy. Bruxelles. Mémoires Couronnés et Mémoirs des Savants Étrangers, Publiés par l'Académie Royale des Sciences et Belles-Lettres de Bruxelles. 4 to. Brussels.

Mém. Div. Sav. Acad. Sci. Mémoires Présentés par Divers Savants à l'Académie des Sciences de l'Institut de France. Paris.

Mém. Divers Sav. St. Petersbourg Acad. Mémoirs Présentés a l'Académie Impériale des Sciences de St. Petersbourg par Divers Savants et lus dans ses Assemblées. St. Petersbourg (1831–59).

Mem. Geol. Surv. Memoirs of the Geological Survey. Peiping, Calcutta.

Mem. Inst. Chem. Acad. Sci. U.S.S.R. Memoirs of the Institute for Chemistry, Academy of Science of the Ukrainian S.S.R.

Mem. Inst. Lombard. Memorie Reale Institute Lombardo di Scienze e Lettere. Milan.

Mém. Mus. Hist. Nat. Mémoires du Muséum d'Histoire Naturelle. Paris.

Mém. Poudres. Mémoires des Poudres et Salpêtres. Paris.

Mem. Proc. Chem. Soc. Memoirs and Proceedings. The Chemical Society. London.

Mem. Ryojun Coll. Eng. Memoirs of the Ryojun College of Engineering. Ryojun, S. Manchuria.

Mém. Soc. Arceuil. Mémoires de Physique et de Chimie de la Societe d'Arceuil. Paris.

Mém. Soc. Imp. Nat. Moscou. Mémoires de la Société Imperiale des Naturalistes de Moscou. Moscow.

Mém. Soc. Lille. Mémoires de la Société Royale des Sciences, de l'Agriculture et des Arts, de Lille. Lille.

Mém. Soc. Phys. Nat. (Geneva). Mémoires de la Société de Physiques et d'Histoire Naturelle de Genève. Geneva.

Mém. Soc. Roy. Sci. Liége. Société Royale des Sciences de Liége. Mémoirs. Brussels.

Mém. Soc. Russe Min. Mémoires de la Société Russe de Minéralogie. Moscow.

Mém. Soc. Sci. Phys. Nat. Bordeaux. Mémoires de la Société des Sciences Physique et Naturelles de Bordeaux. Bordeaux.

Mem. Soc. Spettroscop. Memorie della Società degli Spettroscopisti Italiana. Catania.

Mém. Soc. Vaud. Mémoires de la Société Vaudoise des Sciences Naturelles. Lausanne.

Messenger of Math. Messenger of Mathematics. Cambridge.

Metal Ind. (London). The Metal Industry and the Iron Foundry. London.

Metal Ind. (New York). The Metal Industry. New York.

Metal Progr. Metal Progress. Cleveland, Ohio.

Metal Trans. Metal Transactions. London.

Metal Treatment. London.

Metals and Alloys. Easton, Pa.

Metals Tech. Metals Technology. American Institute of Mining and Metallurgical Engineers. Technical Publication. New York.

Met. Chem. Eng. Metallurgical and Chemical Engineering. New York.

Met. Periodic Rev. Metallgesellschaft Periodic Review.

Metall u. Erz. Metall und Erz. Halle.

Metallbörse. Berlin.

Metallforsch. Metallforschung. Stuttgart.

Metallographist. Boston.

Metallurgia. Manchester.

Metallurgia Italiana. Milan.

Metallurgie. Halle.

Metallwirtsch. Metall-Wirtschaft, Wissenschaft, Technik. Berlin.

Meteorol. Z. Meteorologische Zeitschrift. Brunswick.

Metody Issl. Keram. Mat.

Mfg. Chem. Manufacturing Chemist, and Pharmaceutical, Cosmetic and Photographic Trade Journal. London.

Mikrobiologiya. Moscow.

Mikrochem. Mikrochemie. Vienna.

Mikrochim. Acta. Mikrochimica Acta.

Min. Agr. Dept. N.P. Min. Ministério da Agricultura, Departmento Nacionale da Producão Mineral. Rio de Janeiro.

Min. and Met. Invest. U.S. Ber. Mines Carnegie Inst. Boards. Mining and Metallurgical Investigations under the Auspices of the U.S. Bureau of Mines. Carnegie Institute of Technology and Mining and Metallurgical Advisory Boards. Pittsburg, Pa.

Min. Mag. Mining Magazine. Denver, Colorado.

Min. Petr. Mitt. Mineralogische und Petrographische Mitteilungen. Leipzig, Vienna.

Miner. Ind. Mineral Industry. New York.

Miner. Mag. Mineralogical Magazine and Journal of the Mineralogical Society. London.

Mineracão e Mat. (Rio de J.). Mineracão e Metalurgia (Rio de Janeiro).

Mineral. Syr'. Mineral'noe Syr'e. Moscow.

Mining and Met. Mining and Metallurgy. New York.

Mining Mag. Mining Magazine. London.

Missouri Agr. Exptl. Sta. Ann. Rep. Missouri Agricultural Experimental Station. Annual Report.

Mitt. Chem. Forsch. Inst. Ind. Österr. Mitteilungen des Chemischen Forschungs-Institutes den Industrie Österreichs. Vienna.

Mitt. K. Wilh. Inst. Eisenforsch. Mitteilungen aus dem Kaiser Wilhelm-Institut für Eisenforschung Düsseldorf. Düsseldorf.

Mitt. Kali-Forsch. Anst. Mitteilungen der Kali-Forschungs-Anstalt.

Mitt. Kältestechn. Inst. Karlsruhe. Mitteilungen des Kältestechnischen Instituts. Karlsruhe.

Mitt. Kgl. Materialsprüfungsamt. Mitteilungen aus dem Königlichen Materialsprüfungsamt zu Gross-Lichtenfelde. Berlin-Dahlem.

Mitt. Lab. Preuss. Land. Mitteilungen aus den Laboratorien der preussischen geologischen Landesanstalt.

Mitt. Lebensm. Hyg. Mitteilungen aus dem Gebiete der Lebensmitteluntersuchung und Hygiene. Bern, Switz.

Mitt. Materialsprüfungsamt K. Wilh. Inst. Metallforsch. Mitteilungen aus dem Materialsprüfungsamt und dem Kaiser Wilhelm-Institut für Metallforschung zu Berlin-Dahlem. Berlin.

Mitt. Reichsinst. Forst. u. Holz. Mitteilungen des Reichsinstitutes fur Forst- und Holzwirtschaft.

Mon. Pétrole Roumain. Moniteur du Pétrole Roumain. Bucharest.

Mon. Sci. Moniteur Scientifique du Docteur Quesneville. Paris.

Monatsh. Monatshefte für Chemie und verwandte Teile anderer Wissenschaften Vienna.

Monatsh. Math. Phys. Monatshefte für Mathematik und Physik. Vienna.

Monde Ind. Monde Industriel. Ghent.

Month. Nat. Roy. Astron. Soc. Monthly-Notices of the Royal Astronomical Society. London.

Münch. Med. Woch. Münchener Medizinische Wochenschrift. Munich, Ger.

Munic. Eng. Municipal Engineering. Chicago.

Munic. Eng. Sanit. Record. Municipal Engineering, Sanitary Record and Municipal Motor. London.

Munich. Ber. Sitzungsberichte der Königlichen Bayerischen Akademie der Wissenschaften zu München Mathematisch-Physikalische Klasse. Munich.

N. Engl. J. Med. New England Journal of Medicine. Boston, Mass.

N.J. der Phys. Neues Journal der Physik. Leipzig.

N. Jahrb. Min. Jahrbuch für Mineralogie, Geologie und Paläontologie. Stuttgart.

N. Jahrb. Min. Abhl. Neues Jahrbuch für Mineralogie. Abhandlungen. Section A. Stuttgart.

N. Jahrb. Min. B. Bd. Neues Jahrbuch für Mineralogie etc. Beilage Band. Stuttgart.

N. Jahrb. Min. Monatsh. Neues Jahrbuch für Mineralogie. Monatsheft. Stuttgart.

N. Mém. Acad. Berlin. Nouveaux Mémoires de l'Académie Royale des Sciences et des Belles-Lettres de Berlin. Berlin (1770–86).

N.N.E. National Nuclear Energy Series, Manhatten Project Technical Station New York.

N.Y. State Med. J. New York State Journal of Medicine. Easton, Pa.

N. Zeal. J. Sci. Tech. New Zealand Journal of Science and Technology. Wellington.

Nachr. Ges. Wiss. Göttingen. Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen. Göttingen.

Nachr. Phys. Chem. Lab. Semsoinsés. Nachrichten von der Physikalische-Chemische Laboratory. Semsoinsés.

Nanking J. Nanking Journal. Nanking.

Nat. Petrol. News. National Petroleum News. Cleveland, Ohio.

Natural Gas and Gasoline J. Natural Gas and Gasoline Journal. Buffalo.

Nature. London.

Naturwiss. Die Naturwissenschaften. Berlin.

Naturwiss. Rundsch. Naturwissenschaftliche Rundschau. Brunswick.

Natuurw. Tijdschr. Natuurwetenschappelijk Tijdschrift. Ghent.

Nederl. Tijdschr. Geneeskunde. Nederlandsch Tijdschrift voor Geneeskunde. Amsterdam.

Nederl. Tijdschr. Natuurkde. Nederlandsch Tijdschrift voor Naturkunde. The Hague, Holland.

Neft.

Nernst Festschr. Nernst Festschrift.

New Mex. Mines Min. Res. New Mexico, Bureau of Mines and Mineral Resources, Bulletin. Sorocco, N.M.

New Phytol. New Phytologist. London, New York.

New Zealand J. Agr. New Zealand Journal of Agriculture. Wellington.

New Zealand J. Sci. Tech. New Zealand Journal of Science and Technology. Dunedin.

Nicholson's J. Nicholson's Journal. London.

Nippon Kin. Gakkai-Shi. Nippon Kinzoku Gakkai-Shi. Sendai City, Japan.

Nitrocellulose. Berlin.

Nord. Kjemi. Nordiske Kjemikermøte. 4th Meeting, Oslo, 1932.

Nord. Med. Nordisk Medicin. Stockholm.

Norg. Geol. Undersökels. Norges Geologiske Undersökelse. Oslo.

Norsk Geol. Tijdsskr. Norsk Geologisk Tidsskrift. Oslo.

Norsk Mag. Laegev. Norsk Magasin for Laegevidenskapen.

Northwest Sci. Northwest Science. Moscow, Idaho.

Noticias Farm. Noticias Farmacêuticas. Coimbra, Portugal.

Nouv. Mém. Acad. Berlin. See *N. Mem. Acad. Berlin.*

Nouv. Mém. Soc. Imp. Nat. Moscou. Société Impériale des Naturalistes de Moscou. Nouveaux Mémoires. Moscow.

Nova Acta Leopold. Nova Acta Academiae Caesareae Leopoldina-Carolinae Germanicae Naturae Curiosorum. Halle.

Nova Acta Soc. Reg. Uppsal. Nova Acta Regiae Societatis Scientiarum Upsaliensis. Uppsala.

Novi Comment. Acad. Petropol. Novi Commentarii. Académie Impériale des Sciences de St. Petersbourg. St. Petersburg (1747–75).

N.S.A. Nuclear Science Abstracts.

Nucleonics. New York.

Nuov. Cim. Il Nuovo Cimento. Pisa and Bologna.

Obs. sur la Phys. Observations sur la Physique, sur l'Histoire Naturelle et sur les Arts. Paris.

Ofv. Finska Vet. Soc. Förhl. Ofversigt af Finska Vetenskaps-Societetens Förhandlingar. Helsingfors (Helsinki).

Oefversigt af K. Vetensk. Akad. Förhandl. Oefversigt af K. Vetenskaps Akademiens Förhandlingar. Stockholm.

Ohio Conf. Water Purif. 16th Ann. Rep. 1936. Ohio Conference on Water Purification. 16th Annual Report, 1936.

Ohio Eng. Expt. Stat. Bull. Ohio State University. Engineering Experiment Station Bulletin. Columbus, Ohio.

Ohio J. Sci. Ohio Journal of Science. Columbus, Ohio.

Ohio State Univ. Eng. Expt. Stat. News. Ohio State University. Engineering Experiment Station News. Columbus, Ohio.

Ohio State Univ. Stud. Ohio State University Studies. Columbus, Ohio.

Oil and Soap. Chicago.

Oil Ind. U.S.S.R. Oil and Fat Industry. Moscow.

Oil Gas J. Oil and Gas Journal. Tulsa, Oklahoma.

Öl u. Kohle. Öl und Kohle. Berlin.

Oroznenskii Neft.

O.R.N.L. Oak Ridge National Laboratory. Reports.

Österr. Chem. Ztg. Österreichische Chemiker-Zeitung. Vienna.

Onnes Festschr. Onnes Festschrift. London, 1922

Org. Chem. Ind. U.S.S.R. The Organic Chemical Industry. Moscow.

Orv. Lap. Nep. Orvosok Lapja Népegészségugy.

Osiris. Bruges.

Ov. K. Dansk. Videns. Selsk. Forhl. Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlinger. Copenhagen.

Ostwald's Klassiker. Ostwald's Klassiker der exakten Wissenschaften. Leipzig.

Pacific Chem. Met. Ind. Pacific Chemical and Metallurgical Industries.

Pacific Pulp Paper Ind. Pacific Pulp and Paper Industry. Seattle, Wash.

Paliva a Voda. Prague.

Paper. New York.

Paper Mill. Paper Mill and Wood Pulp News. New York.

Paper Mill News. New York.

Paper Trade J. Paper Trade Journal. New York, Chicago.

Pedology U.S.S.R. Moscow.

Periodico Minerale. Periodico di Mineralogia. Rome.

Pests. Pests and their Control. Kansas City, Mo.

Petrol. Refiner. Petroleum Refiner. Houston, Tex.

Petroleum (German) Petrol. Z. Petroleum Zeitschrift fur die gesamte Interesse der Mineralöl-Industrie. Berlin.

Petroleum. London.

Pharm. Acta Helv. Pharmaceutica Acta Helvetiae. Zurich.

Pharm. J. Pharmaceutical Journal. London.

Pharm. Tijd. Neder. Ind. Pharmaceutisch Tijdschrift voor Nederlandsch-Indie.

Pharm. Weekbl. Pharmaceutisch Weekblad voor Nederland. Amsterdam.

Pharm. Ztg. Pharmazeutische Zeitung. Hamburg.

Pharmacia. Estonia.
Pharmazie. Berlin.
Phil. Mag. Philosophical Magazine. London.
Phil. Trans. Philosophical Transactions of the Royal Society. London. Section A unless B stated.
Phil. Trans. Abdgd. Philosophical Transactions. 18 vols., London, 1809.
Philipp. J. Sci. Philippine Journal of Science. Manila.
Philips Research Rep. Philips Research Reports. Eindhoven.
Philips Technical Review. Eindhoven.
Photogr. J. Photographic Journal. London.
Phys. Ber. Physikalische Berichte. Brunswick.
Phys. Regel. Ber. Die Physik in regelmässigen Berichten. Leipzig.
Phys. Rev. Physical Review. Ithaca, N.Y., Lancaster, Pa.
Phys. Rev. Suppl. Physical Review Supplement. Minneapolis.
Phys. Z. Physikalisch Zeitschrift. Leipzig.
Phys. Z. Sowjet. Physikalische Zeitschrift der Sowjetunion.
Physica. The Hague, Holland.
Physical Memoirs (Phys. Soc.). Physical Memoirs. Published by the Physical Society. London.
Physics. Minneapolis.
Phytopathology. New Haven, Conn.
Plant Physiol. Plant Physiology. Lancaster, Pa.
Plastica. Delft.
Polytechn. Weekbl. Polytechnisch Weekblad. Amsterdam.
Poultry Sci. Poultry Science. Menasha, Wis.
Powder Met. Bull. Powder Metallurgy Bulletin. Yonkers, N.Y.
Power. New York.
Power Generation. New York.
Power Works Engr. Power and Works Engineer. London.
Praktika Akad. Athenon. Praktika tes Akademias Athenon. Athens.
Praktiký Lékař.
Presse Méd. Presse Médicale. Paris.
Priroda. Leningrad.
Problemy Endokrinol. Problemy Endokrinologii
Problems Sov. Geol. Problems of Soviet Geology. Leningrad, Moscow.
Proc. Acad. Sci. Amst. Proceedings of the Royal Academy of Sciences of Amsterdam. Amsterdam.
Proc. Amer. Acad. Proceedings of the American Academy of Arts and Sciences. Boston.
Proc. Amer. Gas Assoc. Proceedings of the American Gas Association. New York.
Proc. Amer. Petrol. Inst. Proceedings of the American Petroleum Institute. New York.
Proc. Amer. Phil. Soc. Proceedings of the American Philosophical Society. Philadelphia.
Proc. Amer. Soc. Animal Production. Proceedings of the Annual Meeting of the American Society of Animal Production. Illinois.
Proc. Amer. Soc. Hort. Sci. Proceedings of the American Society for Horticultural Science. Ithaca, N.Y.
Proc. Amer. Soc. Testing Mat. Proceedings of the American Society for Testing Materials. Easton, Pa.
Proc. Amer. Wood-Pres. Assoc. Proceedings of the American Wood-Preservers' Association. Washington.
Proc. Brit. Assoc. Refrig. Proceedings of the British Association of Refrigeration. London.
Proc. Brit. Inst. Refrig. Proceedings of the British Institute of Refrigeration. London.

Proc. Cambr. Phil. Soc. Proceedings of the Cambridge Philosophical Society. Cambridge.

Proc. Chem. Soc. Proceedings of the Chemical Society. London.

Proc. Durham Phil. Soc. Proceedings of the Durham Philosophical Society. Durham.

Proc. Edin. Math. Soc. Proceedings of the Edinburgh Mathematical Society. Edinburgh.

Proc. Imp. Acad. Japan. Proceedings of the Imperial Academy of Japan. Tokyo.

Proc. Indian Acad. Proceedings of the Indian Academy of Sciences. Bangalore.

Proc. Indian Assoc. for Cultivation of Science. Proceedings of the Indian Association for the Cultivation of Science. Calcutta.

Proc. XV Indian Sci. Congr. Proceedings of the XV Indian Science Congress. Calcutta.

Proc. Inst. Civ. Eng. Proceedings of the Institution of Civil Engineers. London.

Proc. Inst. Mech. Eng. Proceedings of the Institution of Mechanical Engineers. London.

Proc. Inst. Met. Div. Amer. Inst. Min. Met. Eng. Proceedings of the Institute of Metals Division. American Institute of Mining and Metallurgical Engineers. New York.

Proc. Intern. Assoc. Testing Mat. Proceedings of the International Association for Testing Materials. London.

Proc. XI Int. Congr. Pure and Appl. Chem. Proceedings of the Eleventh International Congress of Pure and Applied Chemistry. London, 1947.

Proc. Internat. Congr. Refrig. See *Internat. Congr. Refrig.*

Proc. Iowa Acad. Proceedings of the Iowa Academy of Science. Des Moines.

Proc. Japan Acad. Soc. Proceedings of the Japan Academy of Science. Tokyo.

Proc. K. Akad. Wetens. Amsterdam. Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings of the Section of Sciences. Amsterdam.

Proc. Leeds Phil. Soc. Proceedings of the Leeds Philosophical and Literary Society. Leeds.

Proc. London Math. Soc. Proceedings of the London Mathematical Society. London.

Proc. Nat. Acad. Proceedings of the National Academy of Sciences of the United States of America. Washington.

Proc. Nat. Acad. Sci. India. Proceedings of the National Academy of Science, India. Allahabad.

Proc. Nat. Inst. Sci. India. Proceedings of the National Institute of Sciences of India. New Delhi.

Proc. Nutr. Soc. Proceedings of the Nutrition Society. England and Scotland.

Proc. Trans. Nova Scot. Inst. Sci. Proceedings and Transactions of the Nova Scotian Institute of Science. Halifax, N.S.

Proc. Oklahoma Acad. Sci. Proceedings of the Oklahoma Academy of Science. Norman, Oklahoma.

Proc. Pacific Sci. Congr. Pacific Sci. Assoc. Proceedings of the Pacific Science Congress of the Pacific Science Association. Berkeley, Calif.

Proc. Penna. Acad. Proceedings of the Pennsylvania Academy of Sciences. Harrisburg, Pennsylvania.

Proc. Phil. Soc. Glasgow. Proceedings of the Philosophical Society of Glasgow. Glasgow.

Proc. Phys. Soc. Proceedings of the Physical Society. London.

Proc. Phys. Math. Soc. Japan. Proceedings of the Physico-Mathematical Society of Japan. Tokyo.

Proc. Roy. Dublin Soc. The Scientific Proceedings of the Royal Dublin Society. Dublin.
Proc. Roy. Inst. Proceedings of the Royal Institution of Great Britain. London.
Proc. Roy. Irish Acad. Proceedings of the Royal Irish Academy. Dublin.
Proc. Roy. Soc. Proceedings of the Royal Society. London.
Proc. Roy. Soc. Edin. Proceedings of the Royal Society of Edinburgh. Edinburgh.
Proc. Roy. Soc. Med. Proceedings of the Royal Society of Medicine. London, New York.
Proc. Roy. Soc. N.S. Wales. See *J. Proc. Roy. Soc. N.S. Wales.*
Proc. Soc. Appl. Bact. Proceedings of the Society for Applied Bacteriology. London.
Proc. Soc. Chem. Ind. Victoria. Proceedings of the Society of Chemical Industry. Victoria.
Proc. Soc. Exp. Biol. Med. Proceedings of the Society for Experimental Biology and Medicine. New York.
Proc. Soil Sci. Amer. Soil Science Society of America. Proceedings. Ann Harbor.
Proc. State Coll. Wash. Inst. Dairyg. Proceedings of the State College of Washington. Institute of Dairying. Pullman, Wash.
Proc. and Trans. Rhodesia Sci. Assoc. Rhodesia Scientific Association. Proceedings and Transactions. Salisbury, S. Rhodesia.
Proc. Wash. Acad. Proceedings of the Washington Academy of Science. Washington.
Proc. World Eng. Cong. Tokyo 1929. Proceedings of the World Engineering Congress. Tokyo, 1929.
Product Eng. Product Engineering. Albany, N.Y.
Progr. Theor. Phys. Progress of Theoretical Physics. Kyoto.
Prometheus. Leipzig.
Protar. Solothurn, Switz.
Przeglad Chem. Przeglad Chemiczny. Lemberg, Poland.
Przem. Chem. Przemysl Chemiczny. Warsaw.
Pub. Health News. Public Health News.
Publ. Carnegie Inst. Washington. Carnegie Institute of Washington. Publications. Washington.
Publ. Mass. Inst. Technol. Publications from the Massachusetts Institute of Technology. Boston.
Public Works. New York.
Pulp Paper Mag. Can. Pulp and Paper Magazine of Canada. Gardenvale, Canada.
Q.J. Geol. Soc. The Quarterly Journal of the Geological Society of London.
Quart. J. Chem. Soc. Quarterly Journal of the Chemical Society. London.
Quart. J. Expt. Physiol. Quarterly Journal of Experimental Physiology. London.
Quart. J. Indian Chem. Soc. Quarterly Journal of the Indian Chemical Society. Calcutta.
Quart. J. Math. Quarterly Journal of Mathematics. Oxford.
Quart. J. Pharm. Pharmacol. Quarterly Journal of Pharmacy and Pharmacology. London.
Quart. J. Sci. Quarterly Journal of Science. London.
Quart. Rev. Chem. Soc. Quarterly Reviews. The Chemical Society. London.
Quim. e Ind. Quimica e Industria. Sao Paulo.
R.R. Inst. Lombardo. Rendiconti Real Instituto Lombardo di Scienze e Lettere. Milan.
Rapport Conseil Phys. Solvay. See *Conseil Solvay.*

Razvedka Nedr. Moscow.

Rec. Trav. Chim. Recueil des Travaux Chimiques des Pays-Bas. Amsterdam.

Recherche Aéron. La Recherche Aéronautique. Paris.

Recherches et Inventions. Paris.

Records of General Sci. Records of General Science. London.

Refrig. Eng. Refrigerating Engineering. New York.

Rekonstruktsiya Tekstil. Prom. Rekonstruktsiya Tekstil'noi Promyshlennosti. Moscow.

Rend. Accad. Fis. Mat. Napoli. Rendiconti dell'Accademia delle Scienze. Fisische e Matematiche Classe della Società Reale de Napoli. Naples.

Rend. Ist. Lomb. Sci. Rendiconti dell'Istituto Lombardo di Scienze e Lettere. Milan.

Rend. Ist. Sanit. Pub. Rendiconti Istituto di Sanita Publica. Rome.

Rend. Ist. Super. Sanità. Rendiconti Istituto Superiore di Sanità. Rome.

Rend. Soc. Min. Ital. Rendiconti della Società Mineralogica Italiana. Milan.

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Repert. Phys. Repertorium der Physik. Munich.

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Rev. Acad. Cienc. Madrid. Revista de la Real Academia de Ciencias. Madrid.

Rev. Can. Biol. Revue Canadienne de Biologie. Montreal.

Rev. Cienc. Apl. Revista de Ciencia Aplicada. Madrid.

Rev. d'Acoustique. Revue d'Acoustique. Paris.

Rev. de Métall. Revue de Métallurgie. Paris.

Rev. Esp. Fisiol. Revista Espanola de Fisiologia. Barcelona.

Rev. Fac. Agron. Revista de la Facultad de Agronomica, Universidad de la Republica. Montevideo.

Rev. Fac. Cienc. Córdoba. Revista de la Facultad de Ciencias Médicas de la Universidad Nacional de Córdoba. Córdoba.

Rev. Fac. Cienc. Quim. Revista de la Facultad de Ciencias Quimicas (Universidad Nacional de La Plata). La Plata, Arg.

Rev. Fac. Quim. Ind. Agr. Revista de la Facultad de Quimica Industrial y Agricola (Universidad Nacional del Litoral, Santa Fé, Arg.). Santa Fé, Arg.

Rev. Fac. Sci. Istanbul. Revue de la Faculté des Sciences de l'Université d'Istanbul. Istanbul, Turkey.

Rev. Farm. (B.A.). Revista Farmacéutica (Buenos Aires).

Rev. Gén. Coll. Revue Générale des Colloides. Paris.

Rev. Gén. Froid. Revue Générale du Froid. Paris.

Rev. Gén. Mat. Color. Revue Générale des Matières Colorantes de la Teinture, de l'Impression, du Blanchiment et des Apprêts. Paris.

Rev. Gén. Sci. Revue Générale des Sciences Pures et Appliquées. Paris.

Rev. Ind. Minérale. Revue de l'Industrie Minérale. Paris.

Rev. Inst. Franç. Pét. Revue de l'Institut Français de Pétrole. Paris.

Rev. Méd. Buenos Aires. Revista Médico-quirúrgica de Patologia Femenina. Buenos Aires.

Rev. Mod. Phys. Reviews of Modern Physics. Lancaster, Pa.

Rev. Obras Sanit. Nacion (Buenos Aires). Revista de Obras Sanitarias de la Nacion (Buenos Aires).

Rev. Opt. Revue d'Optique, Théorique et Instrumentale. Paris.

Rev. Philosoph. Revue Philosophique. Paris.

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Rev. Prod. Chim. La Revue des Produits Chimiques. Paris.

Rev. Pure & Appl. Chem. Reviews of Pure and Applied Chemistry. Melbourne, Australia.

Rev. Quim. Ind. Revista de Quimica Industrial (Buenos Aires/Rio de Janeiro).

Rev. Sanidad Militar. Revista de Sanidad Militar. Cuba.

Rev. Sci. Revue Scientifique. Paris.

Rev. Sci. Instr. The Review of Scientific Instruments. Lancaster, Pa.

Rev. Soc. Argentina Biol. Revista de la Sociedad Argentina de Biologia. Buenos Aires.

Rev. Soc. Venezolana Quim. Revista de la Sociedad Venezolana de Quimica. Caracas, Venezuela.

Rev. Teh. A.G.I.R. Revistele Tehnice A.G.I.R. (Asociatia Generalǎ a Inginerilor din R.P.R. (Républica Populara Rômana)). Bucharest, Rumania.

Rev. Univ. Mines. Revue Universelle des Mines. Liége.

Rev. Univ. Zaragoza. Revista Universidad de Zaragoza. Saragossa, Spain.

Rheol. Bull. Rheology Bulletin. New York.

Ric. Scient. Ricos. Ricerca Scientifica e Ricostruzione. Rome.

Ricerca Sci. La Ricerca Scientifica. Rome.

Richerche de Ingegneria. Rome.

Richerche Spettroscop. Richerche Spettroscopiche, Laboratorio Astrofisico della Specola Vaticana. Rome.

Riv. Tec. Ferrovie Ital. Rivista Tecnica delle Ferrovie Italiane. Rome.

Riv. Fis. Mat. Sci. Nat. Rivista de Fisica, Matematica e Scienze Naturale. Pavia.

Riv. Ital. Ess. Profumi. Rivista Italiana delle Essenze e Profumi. Milan.

Rivista Nuov. Cim. Rivista del Nuovo Cimento. Bologna.

Roczn. Chem. Roczniki Chemji. Warsaw.

Rozpravy. Rozpravy České Akademie Ved a Uměni. Prague.

Rubber Chem. Tech. Rubber Chemistry and Technology. Akron, Ohio.

S. Afr. J. Sci. South African Journal of Science. Johannesburg.

S. Afr. Med. J. South African Medical Journal. Capetown.

S. Afr. Mining and Eng. South African Mining and Engineering Journal. Johannesburg.

Sabens Växtskydd.

Safety in Mines Res. Board. Safety in Mines Research Board Papers. London.

Samml. Chem.- u. Chem.-Techn. Vorträge. Sammlung chemischer- und Chemisch-technischer Vorträge. Stuttgart.

Samml. v. Vergift. Sammlung von Vergiftungsfällen. Berlin-Charlottenburg.

Sbornik Česk. Akad. Zemědělsky. Sbornik Česke Akademie Zemědělsky. Prague.

Sbornik Nauk. Sbornik Nauchynkh Rabot Laboratoriĭ Metallofisiki Akademya Nauk Ukrain'skoi S.S.R.

Schweiz. Min. Petr. Mitt. Schweizerische Mineralogische und Petrographische Mitteilungen. Zurich.

Schweiz. Z. Path. u. Bakt. Schweizerische Zeitschrift für Pathologie und Bakteriologie. Basle, Switz.

Sci. Abstr. Science Abstracts. London.

Sci. Agr. Scientific Agriculture. Ottawa, Can.
Sci. and Culture. Science and Culture. Calcutta.
Sci. Japan. Science. Tokyo, Japan.
Sci. Mag. Chem. Cath. Katerinoslav. Scientific Magazine of the Chemical Catheder of Katerinoslav.
Sci. Pap. Inst. Phys. Chem. Res. Tokyo. Scientific Papers of the Institute of Physical and Chemical Research. Tokyo.
Sci. Proc. Roy. Dublin Soc. Scientific Proceedings of the Royal Dublin Society. Dublin.
Sci. Progr. Science Progress. London.
Sci. Rep. Moscow State Univ. Scientific Reports of Moscow State University. Moscow.
Sci. Rep. Nat. Tsing Hua Univ. Science Reports of the National Tsing Hua University. Peiping, China.
Sci. Rep. Tokyo Bunrika Daigaku. Tokyo Bunrika Daigaku. Science Reports. Section A. Tokyo.
Sci. Rep. Tôhoku Imp. Univ. Science Reports of the Tôhoku Imperial University. Tokyo.
Science. Lancaster, Pa.
Scientia. Milan.
Scient. American Suppl. The Scientific American Supplement. New York.
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Scientific Memoirs (Taylor). Scientific Memoirs. Edit. Taylor. London, 1836–53.
Scripta Med. Facultat. Med. Univ. Masaryk. et Palack. Scripta Medica Facultatum Medicinae Universitatis Masarykianae et Palackyanae. Brno, Czech.
Seifen-Öle-Fette-Wachse. Augsburg, Ger.
Semana Med. La Semana Médica. Buenos Aires.
Sewage & Ind. Wastes. Sewage and Industrial Wastes. Champaign, Ill.
Sewage Works J. Sewage Works Journal. Champaign, Ill.
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Siebert Festschr. (Hanau). Siebert Festschrift. Hanau.
Sitz. Akad. Wiss. Wien. Sitzungsberichte der Akademie der Wissenschaften in Wien, Mathematisch-naturwissenschaftliche Klasse. Vienna.
Sitz. Preuss. Akad. Wiss. Sitzungsberichte der preussischen Akademie der Wissenschaften, Physikalisch-mathematische Klasse. Berlin.
Sitzb. Naturforsch. Ges. Rostock. Sitzungsberichte und Abhandlungen der naturforschenden Gesellschaft zu Rostock. Rostock.
Sitzb. Phys. Ökonom. Ges. Königsberg. Sitzungsbericht der physikalisch-ökonomische Gesellschaft zu Königsberg. Königsberg.
Skand. Arch. Physiol. Skandinavisches Archiv für Physiologie. Stockholm, Swed.
Skrift. Norsk. Videns. Akad. Skrifter utgitt av det Norske Videnskaps-Akademi i Oslo. Matematisch-Naturvidenskapelig Klasse. Oslo.
Smithsonian Contributions to Knowledge. Smithsonian Institution. Washington.
Smithsonian Misc. Coll. Smithsonian Miscellaneous Collections. Smithsonian Institution. Washington.
Soap Sanit. Chem. Soap and Sanitary Chemicals. New York.
Soc. Sci. Fenn. Comm. Phys.-Mat. Societas Scientiarum Fennica, Commentationes Physico-Mathematicae. Helsinki, Fin., Copenhagen.
Soc. Franç. Phys. Séances. Société Française de Physique. Bulletin des Séances. Paris, 1902–10.
Soil Sci. Soil Science. Baltimore.
Sow. Phys. Z. Physikalische Zeitschrift der Sowjetunion. Moscow.

Spec. Pap. Geol. Geological Society of America. Special Papers. New York.

Spec. Rep. Food Invest. Board, D.S.I.R. Food Investigation Board Department of Scientific and Industrial Research. Special Report. London.

Spectrochim. Acta. Spectrochimica Acta. London, New York.

Spirto-Vodochnaya Prom. Spirto-Vodochnaya Promyshlennost. Moscow.

Spisy Vydá. Spisy Vydávané Přirodovǎdeckou Fakultou University Karlovy. Prague.

Sprechsaal. Coburg.

Stahl u. Eisen. Stahl und Eisen. Düsseldorf.

Steel Processing. Osceola Mills, Pa., Pittsburgh, Pa.

Stomatologiya. Moscow.

Süddeut. Apoth. Ztg. Süddeutsche Apotheker Zeitung. Stuttgart, Ger.

Sugar. New York.

Sulzer Tech. Rev. Sulzer Technical Review. Winterthur, Switz., New York.

Sum. Kin. Kog. Sumitemo Kinzoku Kogyo Kenkyu Hokoku. Osaka, Japan.

Suomen Kemist. Suomen Kemistilehti. Helsinki.

Surgery. St. Louis, Mo.

Surgery, Gynecol. Obstet. Surgery, Gynecology and Obstetrics with International Abstracts of Surgery. Chicago, London.

Surveyor. Surveyor and Municipal and County Engineer. London.

Svensk Bot. Tid. Svensk Botanisk Tidskrift. Stockholm.

Svensk Farm. Tid. Svensk Farmaceutisk Tidskrift. Stockholm.

Svensk Kem. Tid. Svensk Kemisk Tidskrift. Stockholm.

Svensk Mejeritidn. Svenska Mejeritidningen. Malmo, Swed.

Svensk Papperstidn. Svensk Papperstidning. Stockholm.

Sverige. Geol. Undersokn. Sveriges Geologiske Undersökning. Arsbok. Stockholm.

Tappi. New York.

Tech. Sanit. et Municip. Technique Sanitaire et Municipale. Paris.

Techn. Ind. Schweiz. Chem. Ztg. Technik und Industrie und Schweizer Chemiker Zeitung. Zürich.

Techn. Phys. U.S.S.R. Technical Physics of the U.S.S.R. Leningrad.

Techn. Rep. Tôhoku Imp. Univ. Technical Reports of the Tôhoku Imperial University. Tokyo.

Technique Moderne. Paris.

Technol. Quart. The Technology Quarterly and Proceedings of the Society of Arts. Massachusetts Institute of Technology. Boston.

Tek. Fören. Finland Föhr. Tekniska Föreningens i Finland. Förhandlingar. Helsingfors (Helsinki).

Tekn. Tidskr. (Kem. Mekanik). Teknisk Tidskrift utgiven av Svenska Teknologföreningen. Upplaga Kemi, Mekanik. Stockholm, Norrköping.

Tekn. Tidsskr. Den Tekniske Forenings Tidsskrift. Copenhagen.

Tekn. Ukeblad. Teknisk Ukeblad. Oslo.

Textile Mfr. Textile Manufacturer. Manchester.

Textile Res. J. Textile Research Journal. Lancaster, Pa.

Thonindustr. Ztg. See *Tonindustr. Ztg.*

Tids. Kjemi. Bergvesen. Tidskrift for Kjemi og Bervesen. Oslo.

Tidsskr. Phys. Chem. Tidsskrift for Physik og Chemi. Copenhagen.

Timberman. The Timberman. Portland, Oregon.

Tonindustr. Ztg. Tonindutrie Zeitung. Berlin.

Trans. Amer. Ceram. Soc. American Ceramic Society. Transactions. Columbus, Ohio.

Trans. Amer. Electrochem. Soc. Transactions of the American Electrochemical Society. New York.

Trans. Amer. Foundrymen's Assoc. Transactions American Foundrymen's Association. Chicago, Ill.

Trans. Amer. Geophys. Union. National Research Council. American Geophysical Union. Transactions. Washington.

Trans. Amer. Inst. Chem. Eng. Transactions of the American Institute of Chemical Engineers. New York.

Trans. Amer. Inst. Elec. Eng. Transactions of the American Institute of Electrical Engineers. New York.

Trans. Amer. Inst. Metals. Transactions of the American Institute of Metals. Buffalo.

Trans. Amer. Inst. Min. Met. Eng. Transactions of the American Institute of Mining and Metallurgical Engineers. New York.

Trans. Amer. Inst. Min. Met. Eng. Inst. Met. Div. Transactions of the American Institute of Mining and Metallurgical Engineers. Institute of Metals Division. New York.

Trans. Amer. Phil. Soc. Transactions of the American Philosophical Society. Philadelphia.

Trans. Amer. Soc. Civil Eng. Transactions of the American Society of Civil Engineers. New York.

Trans. Amer. Soc. Mech. Eng. Transactions of the American Society of Mechanical Engineers. New York.

Trans. Amer. Soc. Metals. Transactions of the American Society for Metals. Cleveland, Ohio.

Trans. Amer. Soc. Steel Treating. Transactions of the American Society for Steel Treating. Cleveland, Ohio.

Trans. Bose Inst. Res. Calcutta. Transactions of the Bose Research Institute. Calcutta.

Trans. Brit. Ceram. Soc. British Ceramic Society. Transactions. Stoke-on-Trent.

Trans. Butlerov Inst. Chem. Tech. Kazan. Transactions of the Butlerov Institute for Chemical Technology of Kazan. Omsk, U.S.S.R.

Trans. Cambr. Phil. Soc. Transactions of ,the Cambridge Philosophical Society. Cambridge.

Trans. Canad. Inst. Min. Met. Transactions of the Canadian Institute of Mining and Metallurgy and of the Mining Society of Nova Scotia. Quebec.

Trans. Chalmers Univ. Techn. Transactions of the Chalmers University of Technology. Gothenburg.

Trans. Connect. Acad. Transactions of the Connecticut Academy of Arts and Sciences. New Haven.

Trans. Electrochem. Soc. Transactions of the Electrochemical Society. Baltimore.

Trans. Faraday Soc. Transactions of the Faraday Society. London.

Trans. Illinois State Acad. Sci. Transactions of the Illinois State Academy of Science. Springfield, Ill.

Trans. Illum. Eng. Soc. Transactions of the Illuminating Engineering Society. Baltimore.

Trans. Inst. Chem. Eng. Transactions of the Institution of Chemical Engineers. London.

Trans. Inst. Chem. Tech. Ivanovo. Transactions of the Institute for Chemical Technology of Ivanovo (U.S.S.R.). Moscow.

Trans. Inst. Min. Eng. Transactions of the Institution of Mining Engineers. London.

Trans. Inst. Min. Met. Transactions of the Institution of Mining and Metallurgy. London.

Trans. Inst. Plastics Ind. Transactions of the Institute of the Plastics Industry. London.

Trans. Inst. Pure Chem. Reagents. Transactions of the Institute of Pure Chemical Reagents. Moscow.

Trans. Inst. Rubber Ind. Transactions of the Institution of the Rubber Industry. London.

Trans. IV Mendeleev Congr. Transactions of the Mendeleev Congress of Theoretical and Applied Chemistry. 4th Congress, Kharkov.

Trans. Kansas Acad. Sci. Transactions of the Kansas Academy of Science. Lawrence, Kan.

Trans. Karpov Inst. Chem. Transactions of the Karpov Chemical Institute.

Trans. Mendeleev Congr. Theoret. Appl. Chem. 6th Congr. Transactions of the Mendeleev Congress of Theoretical and Applied Chemistry. 6th Congress, Kharkov, 1932.

Trans. Nat. Inst. Sci. India. Transactions of the National Institute of Sciences of India. Bangalore.

Trans. Opt. Soc. Transactions of the Optical Society. London.

Trans. Proc. New Zealand Inst. Transactions and Proceedings of the New Zealand Institute. Wellington, N.Z., London.

Trans. Proc. Roy. Soc. New Zealand. Transactions and Proceedings of the Royal Society of New Zealand. Wellington, N.Z., London.

Trans. Roy. Dublin Soc. Scientific Transactions of the Royal Dublin Society Dublin.

Trans. Roy. Soc. Canada. Transactions of the Royal Society of Canada. Toronto.

Trans. Roy. Soc. Edin. Transactions of the Royal Society of Edinburgh. Edinburgh.

Trans. Roy. Soc. S. Africa. Transactions of the Royal Society of South Africa. Cape Town.

Trans. Roy. Soc. S. Austr. Transactions of the Royal Society of South Australia. Adelaide.

Trans. Sci. Inst. Fert. U.S.S.R. Transactions of the Scientific Institute of Fertilizers. U.S.S.R.

Trans. Soc. Mech. Eng. Japan. Transactions of the Society of Mechanical Engineers. Tokyo.

Trans. State Inst. Appl. Chem. U.S.S.R. Transactions of the State Institute for Applied Chemistry. U.S.S.R.

Trav. et Mém. Bur. Internat. Poids et Mes. Travaux et Mémoires du Bureau Internationale des Poids et Mesures. Paris.

Trav. et Mém. Fac. Lille. Travaux et Mémoires de la Faculté des Sciences de l'Université. Lille.

Trav. Inst. Métrol. Stand. U.R.S.S. Travaux de l'Institut de Métrologie et de Standardization de l'U.R.S.S.

Trav. Lab. Biogéochim. Acad. Sci. UR.S.S. Travaux du Laboratoire Biogéochimique de l'Académie des Sciences de l'U.R.S.S.

Trav. Phys. Chim. Soc. Sci. Kharkoff. Travaux de la Section Physico-Chimique de la Société des Sciences Experimentales (a l'Université de Kharkoff). Kharkoff.

Trudui Inst. Prom. Isuiskanii. Trudui Instituta Promyshlennost Isuiskaniĭ.

Trudy Arkhangel'skoga Nauch. Issl. Inst. Trudy Arkhangel'skoga Nauchno-Issledovatel'skogo Instituta.

Trudy Azer. Trudy Azerbaidzhanskogo Neftyanogo Issledovatel'skogo Instituta. Baku, Moscow, U.S.S.R.

Trudy Kharkov. Trudy Khar'kovskogo Khimiko-Tekhnologicheskogo Instituta im. S. M. Kirova. Kharkov, U.S.S.R.

Trudy Leningrad. Teknol. Inst. Trudy Leningradskogo Khimiko-Tekhnologichkogo-Instituta. Leningrad.

Trudy Moskov. Neftyan. Inst. Trudy Moskovskogo Neftyanogo Instituta imeni Akad. I. M. Gubkina. Moscow.

Trudy Sredneaziat. Trudy Sredneaziatskogo Gosudarstvennogo Universiteta. Tashkent, U.S.S.R.

Trudy Voenno-Khoz. Akad. R.K.K.A. im. Molotova.

Trudy Vsesoyuz. Akad.

Trudy Vsesoyuz. Konf. Anal. Khim. Trudy Vsesoyuznoĭ Konferentsii po Analiticheskoĭ Khimii. Moscow, Leningrad.

Tsvetnye Metal. Tsvetnye Metally. Moscow.

Uchen. Zapiski Kazan. Uchenye Zapiski, Kazanskiĭ Gosudarstvennyĭ Universitet imeni V.I. Ul'yanova-Lenina. Kazan, U.S.S.R.

Uchen. Zapiski, Leningrad. Uchenye Zapiski, Leningradskiĭ Gosudarstvennyĭ Pedagogicheskiĭ Institut imeni M.N. Pokrovskogo. Moscow.

Ukrain. Chem. J. Ukrainian Chemical Journal. Kharkov.

Umschau. Frankfurt.

Univ. Mich. Stud. University of Michigan. Studies. Scientific Series. Ann Harbor.

Univ. Nebraska Stud. The University Studies of the University of Nebraska. Lincoln, Nebraska.

Univ. of Wash. Publ. in Fisheries. University of Washington Publications in Fisheries. Seattle, Wash.

Univ. Phil. Nat. Appl. Sci. Bull. University of the Philippines Natural and Applied Science Bulletin. Quezon City, P.I.

Univ. Toronto Studies, Geol. Ser. University of Toronto. Studies. Geological Series. Toronto.

Univ. Wisc. Bull. Eng. Ser. University of Wisconsin. Bulletin. Engineering Series. Madison, Wisc.

Uppsala Univ. Årsskrift. Uppsala Universitets Arsskrift. Uppsala.

U.S. Bur. Fisheries Invest. Rept. United States Bureau of Fisheries, Investigational Report.

U.S Bur. Mines Bull. Bureau of Mines Bulletin. Washington.

U.S. Bur. Mines, Inform. Circ. United States Bureau of Mines, Information Circulars. Washington.

U.S. Dept. Agr. Dept. Circ. United States Department of Agriculture, Department Circulars. Washington.

U.S. Dept. Agric. Techn. Bull. United States Department of Agriculture. Technical Bulletin. Washington.

U.S. Geol. Survey Bull. United States Department of the Interior Geological Survey. Bulletin. Washington.

U.S. Geol. Survey Prof. Paper. United States Department of the Interior. Geological Survey. Professional Papers. Washington.

U.S. Naval Med. Bull. United States Naval Medical Bulletin. Washington.

U.S.P. United States Patent.

U.S. Pub. Health Rep. United States Public Health Reports. Washington.

Uspek. Khim. Uspekhi Khimii. Moscow.

Uspekhi Fis. Nauk. Uspekhi Fisicheskikh Nauk. Moscow.

Veda Prirodui Praha. Prague.

Verhl. d. D. Phys. Ges. Verhandlungen der Deutschen Physikalischen Gesellschaft. Berlin-Charlottenberg.

Verhl. d. Naturforsch. Ges. Basel. Verhandlungen der Naturforschenden Gesellschaft in Basel. Basel.

Verhl. d. Vereins z. Beförd. d. Gewerbfl. Verhandlungen des Vereins zur Beförderung des Gewerbfleisses in Preussen. Berlin.

Verhl. K. Akad. Wetens. Amsterdam. Verhandelingen der Koninklijke Akademie van Wetenschappen. Amsterdam.

Verhl. K.K. Geol. Reichsanst. Wien. Verhandlungen der Königlich-Kaiserlichen Geologischen Reichsanstalt. Vienna.

Verhl. Naturhist.-Med. Vereins Heidelberg. Verhandlungen des Naturhistorischen-Medizinischen Vereins zu Heidelberg. Heidelberg.

Verhl. Phys. Ges. Berlin. Verhandlungen der Physikalischen Gessellschaft zu Berlin. Berlin.

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Vestnik Štát. Geol. Úst. Česk. Vestnik Štátniho, Geologického Ústavu Československé Republiky. Prague.

Vestnik Venerol. i Dermatol. Vestnik Venerologii i Dermatologii. Moscow.

Vet. J. Veterinary Journal. London.

Vierteljahresschr. Naturforsch. Ges. Zürich. Vierteljahresschrift der Naturforschenden Gesellschaft in Zürich. Zürich.

Virginia Med. Monthly. Virginia Medical Monthly. Richmond, Va.

Voennaya Khim. Voennaya Khimiya. Moscow, Leningrad.

Voprosy Pitaniya. Moscow.

Vorrats. u. Lebensmittelforsch. Vorratspflege und Lebensmittelforschung. Berlin-Charlottenberg, Ger., London.

Voy. Challenger Rep. Phys. Chem. Report on the Scientific Results of the Voyage of H.M.S. Challenger during the years 1873-6. London, 1880.

Wärme. Die Wärme. Düsseldorf, Ger.

Wärme- Kälte-Techn. Wärme- und Kälte-Techn. Berlin.

Wasser u. Abwasser. Wasser und Abwasser. Berlin.

Wat. Wks. & Sewerage. Water Works and Sewerage. Chicago.

Wat. Wks. Eng. Water Works Engineering. New York.

Water & Sanit. Water and Sanitation. Toronto.

Water & Sewage. Water and Sewage. Toronto.

Water (Holland). The Hague, Holland.

Western Metals. Los Angeles, Calif.

Westinghouse Eng. Westinghouse Engineer. Pittsburg, Pa.

Wiadomości Chem. Wiadomości Chemiczne. Lodz, Poland.

Wien Anz. Anzeiger der Kaiserlichen Akademie der Wissenschaften zu Wien. Mathematisch-Naturwissenschaftliche Klasse. Vienna.

Wien Ber. Sitzungsberichte der mathematisch-naturwissenschaftliche Klasse der Kaiserlichen Akademie der Wissenschaft zu Wien. Vienna.

Wien. Chem.-Ztg. Wiener Chemiker-Zeitung. Vienna, Austria.

Wien. Med. Woch. Wiener Medizinische Wochenschrift. Vienna, Austria.

Wire Ind. Wire Industry. London.

Wis. Natuurkde. Tijdschr. Wis- en Natuurkundig Tijdschrift. Ghent.

Wiss-Abhl. Wissenschaftliche Abhandlungen.

Wiss. Abhl. K. Normal-Eichungs Kommiss. Wissenschaftliche Abhandlungen der Kaiserlichen Normal-Eichungs Kommission. Berlin.

Wiss. Abhl. Phys.-Tech. Reichsanst. Wissenschaftliche Abhandlungen der Physikalisch-technischen Reichsanstalt. Berlin.

Wiss. Veröff. Siemens-Konzern. Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern. Berlin.

Wiss. Veröff. Siemens-Werken. Wissenschaftliche Veröffentlichungen aus dem Siemens-Werken. Berlin.

Wochbl. Papierfabr. Wochenblatt für Papierfabrikation. Württemberg, Ger.

Yale J. Biol. Med. Yale Yournal of Biology and Medicine. New Haven.

Z. anal. Chem. Zeitschrift für analytische Chemie. Munich.

Z. angew. Chem. Zeitschrift für angewandte Chemie. Leipzig.

Z. angew. Math. Zeitschrift für angewandte Mathematik und Mechanik. Berlin.

Z. angew. Min. Zeitschrift für angewandte Mineralogie. Berlin.

Z. angew. Phys. Zeitschrift für angewandte Physik. Munich.

Z. anorg. Chem. Zeitschrift für anorganische und allgemeine Chemie. Leipzig.

Z. Elektrochem. Zeitschrift für Elektrochemie. Halle.

Z. Elektrochem. angew. phys. Chem. Zeitschrift für Elektrochemie und angewandte physikalische Chemie. Berlin.

Z. Erz. u. Metall. Zeitschrift für Erzbergbau und Metallhüttenwesen. Stuttgart.

Z. f. Chem. Zeitschrift für Chemie. Göttingen.

Z. f. Phys. und verwandte Wiss. Zeitschrift für Physik und verwandte Wissenschaften. Vienna.

Z. Forst- u. Jagdwesen. Zeitschrift für Forst- und Jagdwesen. Berlin.

Z. Geol. Ges. Zeitschrift der Deutschen Geologischen Gesellschaft. Berlin.

Z. ges. exptl. Med. Zeitschrift für die gesamte experimentelle Medizin zugleich Fortsetzung der Zeitschrift für experimentelle Pathologie und Therapie. Heidelberg, Ger., London.

Z. ges. Hyg. Zentralblatt für gesamte Hygiene. Berlin.

Z. ges. Kälte-Ind. Zeitschrift für die gesamte Kälte-Industrie. Berlin.

Z. ges. Naturwiss. Zeitschrift für die gesamten Naturwissenschaften. Halle and Berlin.

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CHAPTER I

FLUORINE

A SURVEY of the literature relating to developments in the chemistry of fluorine which have occurred since 1921 discloses the publication of certain books and review articles which are not cited elsewhere in this chapter. Attention is therefore conveniently directed at this stage to these reviews, as well as to two earlier works of similar character.[1-26]

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SECTION 1.

THE OCCURRENCE, PREPARATION AND MANUFACTURE OF FLUORINE.

By H. R. LEECH

THE OCCURRENCE OF FLUORINE.

GEOCHEMISTRY

Fluorine is very widely disseminated in nature, almost entirely in the combined form. Its occurrence in the free state has been reported and discussed,[1] and these occurrences are associated with the presence of radioactivity, as in the classical case of Wölsendorf fluorspar.[2] A Canadian fluorspar, the radioactivity of which has been measured,[3] was found to contain 15 – 16 p.p.m. of free fluorine. This radioactivity is attributed to the presence of radium, extracted from uranium minerals by fluorine-containing water.[4] On the other hand, the coloration of a Russian fluorspar has been attributed to free calcium.[5]

Spectrographic evidence indicates the existence of fluorine, and affords rough estimates of its abundance, in the sun,[6] stars[7] and nebulae.[8] It is also suggested that certain lines are due to fluorine compounds in the sun and in the stars.[9] On the other hand, a consideration of forbidden transitions casts doubt on the presence of fluorine in certain novae.[10]

In the 3rd Edition of his *Data of Geochemistry*, published in 1916, Clarke gave the average of 112 determinations of the fluorine content of igneous rocks as 0•10%. He believed, however, that fluorine exists in these rocks chiefly as apatite, and as the phosphorus content can be determined more accurately than the fluorine, took the figure for apatitic fluorine corresponding to the average phosphorus content, viz., 0•027%. In the 5th Edition, published in 1924, a figure of 0•030% for the average fluorine content of igneous rocks (which make up more than 90% of the 10 mile crust of the earth) was boldly taken[11] and the reason for this is discussed by Clarke and Washington.[12] The average of fluorine determinations, depending on the manner in which the averaging was carried out, could be between 0•006% and 0•15% fluorine. Perhaps the mean of these, 0•078%, would represent the best average. But, still misled by their assumption that the fluorine is mostly present as apatite, and mistrusting the accuracy of their fluorine determinations, they preferred a figure based on the phosphorus content, and so arrived at 0•030%.

More recent work has shown that the basic assumption, that fluorine in igneous rocks is principally present as apatite, is invalid. Shepherd found that the fluorine content of rocks, based on more than 100 analyses, was about 0•04%, and approximately equal to the chlorine content.[13] Samples from the ocean bottom contained about the same amount of fluorine. Later he reported an average of 0•070% in volcanic rocks, though eruptive lavas may have lost fluorine and give a low figure.[14] Later workers have emphasised the low proportion of fluorine combined as apatite, and the relatively large proportion present in mica, in hornblende, and in fluorite, in

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igneous rocks.[15] Recent work suggests 0·06 – 0·09%,[16] 0·075%,[17] 0·080%[15] of fluorine and emphasises that this exceeds the proportion of chlorine.[17] A recent comprehensive study gives an average of 0·070% of fluorine in igneous rocks, and 0·065% in sedimentary rocks.[18] On the other hand rocks which have undergone weathering have been reported to contain only 0·024% of fluorine and 0·035% of chlorine.[19] In a survey of the situation, the following comparative data have been given[20]

	Fluorine p.p.m.	Chlorine p.p.m.
Igneous rocks, average	600	314
Meteorites, "	28	1000 — 1500

This very great change in the proportions of the two halogens is surprising. The fluorine content of meteorites has not, however, been very thoroughly studied, and it seems possible that they have lost a considerable amount of fluorine by processes of volatilisation which have been noted as occurring in terrestrial volcanic regions.

In the sea, the fluoride content is proportional to the chloride content, the ratio being $7{\cdot}0 \times 10^{-5}$, but surface coastal waters have a rather higher content of fluorine.[21]

In the geochemical cycle[15,18,20,22] there are two active agencies bringing fluorine into circulation, namely rivers and volcanic activity. The fluorine so 'activated' tends to separate out in fluorophosphates, owing to their extreme insolubility, and the fluorine is then returned to the more slow-moving orogenetic cycle. Volcanic gases contain appreciable concentrations of fluorine compounds: thus Shepherd[23] reported 3·61 to 6·20% by volume of fluorine-containing gases. The escape of hydrofluoric acid and silicon tetrafluoride in gases from an Italian fumarole has been reported,[24] and hydrofluoric and hydrochloric acid, as well as aluminium, calcium, and magnesium fluorides, have been found in Russian volcanic gases and sublimates.[25] It has, indeed, been estimated that one volcanic group, the Katmai region, exhales annually 135,000 tons of hydrofluoric acid.[26]

It is suggested that volcanic effusion of hydrofluoric acid has played a large part in the conversion of phosphates to the highly insoluble apatites, and attention has been directed to the accumulation of volcanic products in the neighbourhood ot the principal phosphate deposits in the U.S.A.[27]

MAJOR MINERALS

It is suggested that fluorine brought into circulation by rivers and by volcanic activity tends to separate out as apatite, $Ca_5(PO_4)_3(F,Cl,OH)$, and also that apatite and certain other accessory constituents are the first minerals to separate out in all igneous rocks,[20] and fluorine-containing phosphatic rock is certainly one of the principal modes of occurrence of fluorine in concentrated form. These minerals are very widespread, and are extensively exploited for their phosphorus content, the fluorine being largely wasted. Thus one estimate indicates that in one year, 1928, the quantity of fluorine volatilised in phosphate processing was about 25,000 tons.[28] The fluorine content is rather variable, being between 3 and 4% for continental deposits, but lower for island deposits, and sometimes as low as 0·4%.[29] Considering the ratio ot fluorine to phosphorus pentoxide rather than the fluorine content, it is found that the ratio is in many cases higher than that in fluoroapatite ($Ca_{10}F_2(PO_4)_6$, $F/P_2O_5 = 0{\cdot}0891$); for continental deposits it varies between 0·09 and 0·140. But in crystalline apatite itself the ratio may also be high, varying between 0·0809 and 0·1099, with an average value of 0·0945.[30] Florida phosphates show a ratio of 1·41,[31] and in Russian deposits also a direct relation between the fluorine and phosphorus content has been observed.[32] Sea bottom deposits of phosphorite nodules containing fluoroapatites have been described,[33] and other workers have reported on the analysis of apatites.[34]

It was suggested by Carnot[35] in 1892 that fluorophosphates have been formed by the action of fluorine-bearing water on phosphates. Thus it is found that the fluorine content of fossil bones depends on their age, so that whilst recent horse bones contain less than 0·01% fluorine, fossil bones from the Miocene in Florida contain 1·7 and 2·6% of fluorine.[36] It also suggested that the lower fluorine content of island phosphate deposits is to be attributed to their more recent origin.[30]

The principal source of fluorine for industry is calcium fluoride, CaF_2, which occurs naturally as fluorspar (fluorite). The ores are very widespread, and are worked in many countries.[37] The U.S.A. is the principal consumer and the largest producer The estimated world production figures for fluorspar in 1948 were[38] in short tons:-

U.S.A.	300,956
Mexico	75,381
United Kingdom	71,124
Newfoundland	47,833
Italy	41,000
Germany	37,549
Spain	30,250
* Others	200,000
Approximate Total	800,000

* This figure includes estimates for Russia and the Eastern Zone of Germany, and smaller producers.

An estimate in 1931 gave a world production of 300,000 tons, thus indicating the rapid growth of the fluorine industry.[39] American consumption is 57% for metallurgical industry (largely steel), 26% for chemical industry (conversion to hydrogen fluoride), 10% for glass and ceramics.[38] The economics of the fluorspar industry from the American point of view, and the beneficiation of ores, have been discussed.[40] The American production comes mainly from the States of Illinois (52%), Kentucky (25%), Colorado (8%) and New Mexico (8%), and many detailed descriptions of individual occurrences in these, and in other States, are available.[41]

In Britain, fluorspar occurs in Derbyshire[42] and in the County of Durham.[43] The occurrence and utilisation of fluorspar in France,[44] Belgium,[45] Germany,[46] Italy,[47] and Czecho-slovakia[48] have also been described. There have also been general descriptions of the fluorspar position in U.S.S.R.,[49] China,[50] Japan,[51] Canada,[52] Brazil,[53] South Africa,[54] and Australia.[55] Detailed descriptions have been given of special localities in U.S.S.R.,[56] India,[57] China,[58] Japan,[59] Canada,[60] Brazil,[61] South Africa,[62] and New Zealand.[63]

One fluorine-containing mineral, cryolite, $AlF_3,3NaF$, is known to occur in commercial quantities only at one place, Ivigtut, in Greenland. The ore is mined and several grades are produced by processing and purification treatments.[64]

MINOR MINERALS

Zamboninite was the name given to a mineral $CaF_2,2MgF_2$ found on Mt. Etna, which, it was suggested, has been formed by action of vapours containing fluorine compounds on solutions containing magnesium and calcium.[65] Subsequent *X*-ray examination showed this material to be a mixture of the two known minerals sellaite (MgF_2) and fluorspar.[66] name name ferrucite has been proposed for sodium fluoborate, ($NaBF_4$), identified in the products of fumarole activity at Vesuvius.[67] A complex fluoroaluminate has been found in the lava flow of a Russian volcano, Klyuchevsky, approximating to $NaCaMgAl_3F_{14},4H_2O$, and theretore differing from ralstonite by its higher calcium content.[25]

Mineral occurrences related to apatites have been reported; and sometimes chlorine as well as fluorine may be present[68] whereas the slag mineral steadite is a fluorapatite in which some of the phosphorus has been replaced by silicon.[69] An aluminium iron phosphate containing fluorine and chlorine has been reported from Venezuela,[70] and amblygonite, $LiAlFPO_4$, 0·25 H_2O, as a constituent of a complex mineral from Uganda.[71]

Minor occurrences of fluorspar in complex admixture with other minerals have been reported from many countries.[72]

Fluorine enters into the constitution of a number of minerals found in many localities: tourmaline,[73] topaz,[74] which corresponds closely to $(AlF)_2SiO_4$ and on heating to 1300°C. gives a quantitative yield of silicon tetrafluoride;[75] various micas, and the following:-

Fluoro-annite	$KFe_3^{II}(Al,Si)_3O_{10}F_2$
Fluoro-biotite	$K(Mg,Fe^{II})_3(Al,Si)_3O_{10}F_2$
Fluoro-siderophilite	$KFe_3^{II}[(Al,Fe^{III})Si_3]O_{10}F_2$
Fluoro-lepidomelane	$K(Mg,Fe^{II})_3[(Al,Fe^{III})Si_3]O_{10}F_2$
Fluoro-meroxene[76]	$KMg_3[(Al,Fe^{III})Si_3]O_{10}F_2$
Phlogopite[77]	$K_2O,6MgO,Al_2O_3,6SiO_2,2H_2O$
Lepidolite[78]	$K(Li,Al)_3(Al,Si)_4O_{10}(OH,F)_2$

The chief fluorine bearing mineral in basaltic effusions is amphibole.[79] Fluorine has been reported in minor amounts in sphene,[80] in Chinese brines,[81] in lime,[82] in borate deposits[83] and from various other mineral sources.[84]

Some attention has been paid to the general distribution of fluorine in soil. Russian workers have found from 100 to 300 p.p.m. in dry soil, with an average of 200 p.p.m. of fluorine.[85] American workers have given a wide range of values, from a trace to 7070 p.p.m., with figures generally between 50 and 400 p.p.m.[86] Though soils containing fluorine invariably have apatite among the minerals present, the source of most of the fluorine in normal soils is considered to be the various micas, muscovite, biotite, etc. Fertilisation tends to increase soil fluorine content, but the uptake of fluorine by plants is small.[87] For New Zealand soils, fluorine contents varied between 68 and 540 p.p.m.[88]

Fluorine is also present in coal:[89] Lessing reported not more than 1 p.p.m. of fluorine, present mainly as calcium fluoride, with a ratio of fluorine to chlorine as in sea water.[90] Crossley, however, found up to 175 p.p.m., with an average of 80 p.p.m. of fluorine, in coals from widely different sources, the fluorine being present as fluorapatite and not as fluorspar or cryolite, and bearing no relation to the chlorine content.[91] The direct contact of combustion gases with malt in kiln drying can introduce up to 2 p.p.m. of fluorine into beer.[92] Fluorine has also been reported as a regular constituent of gas liquor.[93] Because of the wide occurrence of fluorine in minor amounts, it may be evolved in the fumes from calcination, e.g. of clay and iron ore, and thus cause toxic effects such as the poisoning of cattle grazing in the vicinity. The presence of fluorine in clay to the extent of 500 p.p.m., and in ironstone to the extent of 1200 p.p.m., and the effects of this on calcination, have been reported by H.M. Alkali Inspector.[94]

WATER

In the last twenty years a considerable interest has developed in the fluorine content of drinking water supplies. It was first observed that there was a correlation between 'mottled enamel' of teeth, and high fluorine content of the water supply. It was later observed that dental caries was much less prevalent where the mottled enamel was endemic, and also that in the region where mottled enamel did not appear dental caries was much more prevalent where the fluoride content was particularly low.[95] Arising from these observations, there now exists an extensive literature on the fluoride content of water supplies all over the world. Most British waters are low in fluorine, with contents usually between 0·1 and 0·5 p.p.m.; figures for well waters occasionally rise to 1 p.p.m., and Maldon, Essex, has 5 p.p.m.[96] For the U.S.A. the extensive results have been presented in the form of a distribution map, and some consideration has been given to the causes of variations.[97] In dry and desert areas the fluorine content of ground waters is high, because of the low rate of leaching. Wide variations occur; frequently the fluorine content is below 1 p.p.m., but higher figures are not unusual, and figures as high as 7 p.p.m. have been reported for S. Carolina,[98] N. Dakota[99] and Alabama [100] Many other results have been reported from the U.S.A.[101] and from every continent.[102] Consideration has been given to the modification of the fluorine content of water supplies. At first the emphasis was on reducing the fluorine content:[103] it has been proposed to treat the water supply with alum;[104] with lime and magnesia, so that most water softening plants are adaptable;[105] with superphosphate and lime;[106] and with alumina and aluminum phosphate.[107] More recently fluoride additions have been made to supplies low in fluorine, and it has even been proposed to vary the addition with the season to allow for the variation in the amount of water drunk.[108]

ORGANIC MATERIALS

The importance of fluorine in dental health has led to many determinations of the amount present in foodstuffs and organic materials. Chinese common salt is reported to contain 0·8 to 54 p.p.m.[109] Vegetation in the neighbourhood of Pittsburgh showed from 9 to 269 p.p.m. of fluorine, the amount increasing as the season advanced, probably owing to accumulation of fluorine-bearing dust.[110] Russian reports indicate 30 to 40 p.p.m. in some vegetable crops and amounts too low (<0·1 p.p.m.) for accurate determination in others.[111] Animal feeding stuffs contained from 1 to 30 p.p.m.[112] Tea leaves contain a relatively high proportion of fluorine, and figures have been reported of 160 – 200 p.p.m.,[113] 60 – 350,[114] 90 – 140.[115] Fluorine is reported to be present in grapes[116] and in wine: in Rhine wines, between 0·06 and 0·5 p.p.m.;[117] in Spanish wines, up to 5 p.p.m.;[118] in Argentine wines, up to 1·75 p.p.m., although of 228 samples 93% had less than 0·5 p.p.m.[119] Higher fluorine content in wines may arise owing to accidental contamination from insecticides in the vineyards, or to deliberate attempts to control bacterial disease.[120] Gelatine normally contains 1 p.p.m.[121] One remarkable report suggests that apricot preserves have in the past caused mass illness owing to fluorine poisoning.[122] Fish, fish pastes, tinned fish and crustacea have what are regarded as rather high fluorine contents, up to 24 p.p.m.[123] A complete analysis of the fluorine distribution in a laying hen has been reported.[124] Numerous other reports have been made.[125]
Moir (1944) gives the following figures,[126] in p.p.m. of fluorine:-

White flour	0·29 – 0·60	(Av. 0·42)
National flour	0·68 – 1·05	(Av. 0·82)
S. R. flour	4·9 – 7·4	(Av. 6·1)
Milk (powder)	0·48 – 0·83	(Av. 0·61)
Tea	107 – 129	(Av. 116)

Beer	0·45, 0·25	Pilchards (canned)	5·8
Corned beef	0·4	Shrimps (canned)	2·4
Egg (dried)	0·3	Milk (evaporated)	0·15
Milk	0·17	Oats (rolled)	0·6
Soya grits	0·6	Spinach powder	70
Peas (split)	0·4	Whisky	0·03

The fluorine content of human bones and teeth is about 0·05%, the fluorine being there in hydroxyapatite.[127] For land animal skeletons the figure is about the same, though for sea animals it is ten times as great, or more; e.g., a figure of 2·84% is reported for shark tooth.[128] Differences between the fluorine contents of dentine and enamel, and between carious and sound teeth, have been reported as follows, the higher fluorine content corresponding with higher fluorine in the drinking water:-

	Low caries		High caries	
	dentine	enamel	dentine	enamel
fluorine:% Ockerse[129]	0·0755	0·0445	0·0258	0·0153
Hoogland[130]	0·02–0·11	0·01–0·02	0·04–0·17	0·01–0·09

McClure[131] on the other hand found no significant difference between sound and carious teeth, and reports 0·0233% of fluorine in dentine, 0·0100% in enamel. The lower fluorine content of enamel has been confirmed by Russian workers[132] and in mildly mottled teeth from Maldon, Essex, where fluorosis is endemic, dentine and enamel respectively contain 0·07 and 0·035% of fluorine.[133] There is a considerable literature on endemic dental fluorosis.[134].

The content of fluorine in human blood has been given as 0·27 to 0·74 p.p.m.[135] When the water-supply fluorine increased from 0·06 to 1·36 p.p.m., the mean blood content increased from 0·014 to 0·040, and the mean urinary fluorine from 0·06 to 1·12 p.p.m.[136]

The general physiological effect of fluorine is dealt with elsewhere: but McClure[137] has reviewed the occurrence of fluorine in animal tissues, and its consequences. An increase in skeletal fluorine content up to twenty times the normal value owing to continual exposure to fluorine-containing rock phosphate has been described.[138] In the disease of sheep known as 'darmous' or 'Moroccan fluorosis' a similar great increase in fluorine content occurs.[139] The increase in fluorine content of human organs in cases of fluorine poisoning has been described.[140]

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THE PREPARATION OF FLUORINE

FORMATION OF FLUORINE BY CHEMICAL REACTION

Whilst fluorine can readily be isolated by electrolysis, it may in certain circumstances be convenient to obtain a quantity of fluorine by simple chemical means. (Fluorine is now commercially available as the compressed gas, in steel cylinders, see page 42). It is also of interest to know where reactions may lead to the liberation of fluorine. Mellor (II, 6) reported numerous attempts to prepare fluorine chemically, and said of wet processes that they were now known to be a wrong line of attack, but that some of the dry processes may have yielded some fluorine. In general the less stable fluorides would be expected to yield fluorine on heating, and attempts were also made to displace fluorine by other halogens, and by oxygen. Moissan suggested that the fluorides of gold or platinum would be suitable sources of fluorine if they could be made by an indirect method not requiring elementary fluorine, and that more complete study of the fluorides of manganese, lead, copper, and cerium, might give valuable results. Brauner's suggestion in 1881 that fluorine was probably formed by thermal decomposition of lead tetrafluoride or its double salts is frequently quoted. It is less well known that this was refuted by Ruff,[1] and that Brauner[2] accepted this refutation. The possibility of making fluorine in this way was throughly investigated by the American team which first introduced the high temperature fluorine cell.[3] The salts K_3HPbF_8 and Na_2PbF_6 were prepared and characterized, and their solubilities determined. The sodium salt is very sensitive to atmospheric moisture, the potassium salt less so, and on heating the latter at 250°C. for 4 hours, the hydrogen fluoride is lost. On further heating the potassium salt at 300°C. there were indications that fluorine was evolved. Although the sodium salt appeared to decompose at a lower temperature, less work was done on it owing to the difficulty of obtaining it in a pure form. It seems, however, that the authors were not very satisfied with the evidence for the liberation of fluorine.

Meyer in 1913 described a process for making the fluoride of trivalent manganese, and the potassium double salt, K_2MnF_5, was readily obtained. On heating the absolutely dry salt fluorine appeared to be split off, and it was concluded that if this preliminary experiment proved to be free from objection, a method of preparing fluorine by purely chemical means was available.[4] It is interesting to note that more recently the action of hydrogen fluoride on manganese dioxide at 450° has been described.[5] No volatile fluoride was formed, and analysis showed that the product was MnF_2. It was assumed that the first product would be the tetrafluoride, which must then have decomposed to difluoride and fluorine, but fluorine would not be observed in the gaseous products owing to its reaction with the water also formed. This is, however, tantamount to saying that oxygen is evolved on heating manganese dioxide in hydrogen fluoride and the equation could be written

$$MnO_2 + 2HF \rightarrow MnF_2 + H_2O + \tfrac{1}{2}O_2.$$

Ginsberg and Holder[6] in 1930 – 1932 studied the fluorotitanates, particularly the potassium salt. On heating in a stream of dry air to temperatures above 500°C. this salt was converted into K_2TiOF_4, and it was concluded that the possibility of hydrolytic reaction had been eliminated, and elementary fluorine must have been formed. The production of fluorine by a somewhat similar process – the decomposition on heating to above 200°C. in oxygen, of complex oxyfluorides of zirconium, hafnium, or titanium – has been patented, and oxygen-evolving compounds, e.g. peroxides, may be used instead

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of free oxygen.[7] Moissan could not obtain platinum tetrafluoride by any reaction other than the attack of fluorine on the metal, and the solid obtained decomposed at red heat into crystalline platinum and fluorine, which was identified by its causing silicon to inflame.[8] On the other hand, Ruff found that the double compounds of platinum tetrafluoride with alkali fluorides could be heated to bright red heat without decomposition.[9] Platinum tetrafluoride has also been prepared recently by Sharpe by the action of bromine trifluoride on platinum tetrachloride,[10] and the compound so prepared has properties identical with those of the compound prepared by Moissan.

Gold was stated by Moissan to be attacked by fluorine; the product, auric fluoride, is volatile, and decomposes at temperatures a little higher than that at which it was formed, giving fluorine and metallic gold.[11] The higher fluorides of the other metals of the platinum group, and of the metals of the palladium group of transition elements, probably behave similarly. Sharpe has also recently shown that bromine trifluoride dissolves gold,[12] and he finally obtained auric fluoride, AuF_3, which only began to decompose rapidly above 500°C., the evolution of fluorine being assumed from the observed action on potassium iodide.

A number of higher fluorides were used during the 1939–45 war as fluorinating agents for the preparation of fluorocarbons (see page 199). These included cobalt trifluoride, silver difluoride, manganese trifluoride, and lead and cerium tetrafluorides. All these require free fluorine for their production, at temperatures up to 350°C., so that in this region, at least, the equilibrium pressure of fluorine must be less than one atmosphere. There was in fact in the work that has been reported little evidence that the equilibrium pressure of fluorine was at all appreciable in the working region. Otto Ruff regarded cobalt trifluoride as a valuable fluorinating agent,[13] but also describes its decomposition when heated in a hard glass tube, in a stream of carbon dioxide, so that at 350° it is converted into the practically pure difluoride.[14] It has also been suggested more recently that when heated in a stream of dry nitrogen to 300–350°C. cobaltic fluoride liberated fluorine.[15]

Argentic fluoride, AgF_2, was first made in 1933.[16] In a general paper in 1937 it was stated that this salt gave an equilibrium pressure of fluorine of one atmosphere at about 450°C.[17] but the authority quoted for this statement does not in fact support it.[18]

Ruff, however, said that the dissociation pressure of argentic fluoride reaches one atmosphere at about 440°C.;[19] he has described the reaction of precipitated silver with fluorine when heated in a fluorspar boat in an electrically heated fluorspar tube,[20] at different temperatures. At 435°C. the product was AgF_2, at 450°, AgF, and it was concluded that the dissociation pressure must be greater that 760 mm. at 450°. (It was noted in this work how resistant copper was to fluorine even at 350°C., but that the presence of a little chlorine in the fluorine caused a very considerable increase in the rate of reaction.) Doubt has been cast on these observations by von Wartenberg,[21] who made a direct determination of the heat of reaction of silver and fluorine, and found

$$Ag + F_2 = AgF_2 + 84{\cdot}5 \text{ kg.-cal.} \pm 1{\cdot}2$$

From existing data, the heat of formation of AgF is 50 kg.-cal. so that

$$AgF + \tfrac{1}{2}F_2 = AgF_2 + 34{\cdot}5 \text{ kg.-cal.}$$

With such a high heat of formation, the salt should be stable at red heat, and the foregoing observations of Ruff and Giese are inexplicable. Silver was heated in an alumina boat in an alumina tube, in a stream of 10% fluorine and 90% nitrogen; after 15 minutes at 550°C., a 100% yield of AgF_2 was obtained. When this compound was heated at temperatures rising from 300° to 700° in the same gas mixture, no loss in weight occurred in 30 minutes. At 650°C. a slight attack on the boat occurred, at 680° the salt softened, and at 700° it was molten and crept over the edge. It was concluded that the melting point was about 690°C. and that at this temperature the dissociation pressure is still less than 0·1 atm. The fluorine used was obtained from a cylinder supplied by I.G. Farbenindustrie, Leverkusen, and when analysed by mercury absorption was found to contain 75% fluorine, 17% nitrogen, and 8% oxygen. Subsequently, the same author said that there was a good deal of misapprehension as to the ease with which higher fluorides decompose.[22] From experimental work similar to that just outlined, he concluded that lead tetrafluoride is stable at red heat, and that manganese trifluoride and cobalt trifluoride have dissociation pressures less than 0·1 atm. at 600°C.

More recently, the decomposition of the alkali metal salts of uranium hexafluoride (e.g. K_3UF_9) in a stream of dry oxygen-free nitrogen at 450°C. has been reported to give some fluorine,[23] and it has been concluded that above 900°C. plutonium tetrafluoride decomposes to the trifluoride and free fluorine, and therefore shows an appreciable dissociation pressure of fluorine ($>10^{-6}$ mm. of mercury).[24] Alkali halides, with free fluorine, are said to give in certain circumstances unstable 'active fluorine' compounds of the form MF_2 and MF_3.[25] The photosensitized decomposition of carbon tetrafluoride has been shown to give rise to free fluorine and an unidentified solid product.[26] All this work should be treated with a certain reserve in the absence of any specific identification of elementary fluorine produced in the reaction. Yet for any given fluoride there must obviously be a temperature at which the equilibrium pressure of fluorine, arising from its partial or complete decomposition, reaches a certain desired value, and the fundamental problem is to find material for the reaction vessel such that it will not react with fluorine produced at the temperature of operation.

Materials resistant to fluorine are essential if trustworthy observations are to be made. Platinum and gold are not very satisfactory materials because of their reaction with fluorine at higher temperatures; nickel is much the best metal to employ and is probably reasonably satisfactory. Moissan carried out his work on the decomposition of platinum tetrafluoride in tubes turned from selected pieces of fluorspar[8] but this is an unreliable material and very sensitive to heat shock. Damiens has described the production of porcelain-like material, in the form of tubes, crucibles etc., from a plastic mass made from precipitated calcium fluoride, which is resistant to temperature shock and almost impermeable,[27] and a furnace using a tube of such material[28] for use with fluorine up to 1000°C. was described. The production of sintered articles in fluorspar has also been described more recently.[29] Ruff has shown that a wide variety of materials can be made into plastic masses and thus into ceramics.[30] Probably the most promising material for use with fluorine at high temperatures is sintered alumina, which has been reported to show no weight change after exposure for many hours to fluorine at 400 – 500°C. and may even be heated for some hours in fluorine at 700°C. without obvious attack.[31] This material was used, for example, to determine the melting point of thallic fluoride, 550°C., in a fluorine atmosphere. With this range of resistant materials, it should be possible to study the thermal decomposition of the less stable fluorides and exchange reactions involving fluorine.

For studies of the thermal conductivity of fluorine, the element has been made by decomposition of chlorine trifluoride.[32] This was passed, from a steel cylinder, into a nickel tube at 700°C. when it was almost completely decomposed into chlorine monofluoride and fluorine. The gases were rapidly cooled at the exit of the nickel tube to minimize recombination, and cooled first by solid carbon dioxide and then by liquid air to condense out chlorine trifluoride and monofluoride. Passage over a nickel spiral at 400°C. converted any residual monofluoride to trifluoride, which was removed by cooling again with solid carbon dioxide and liquid air. The authors do not, unfortunately, give any chemical analysis for the chlorine content of the gas, but state that after long working there was only a slight precipitate in the final liquid air trap, and that the partial pressure of chlorine monofluoride in the fluorine could not have exceeded a few tenths of a mm.

FLUORINE TO 1940

The demonstration by Moissan, in 1886, that elementary fluorine could be isolated by electrolysis, marked the end of a search which had lasted for more than seventy years. But this search, and the properties Moissan was able to disclose, created an impression of great difficulty and danger in making and handling fluorine which persisted for many decades. Thus in the succeeding thirty years there were only some half dozen workers other than Moissan who described the production of fluorine. Attention should, however, be drawn to a patent specification of Poulenc Frères and Meslans[33] at the beginning of the century which embodied many features used in later designs. A cell was developed which, as distinct from Moissan's U-form, was cylindrical, with a diaphragm separating the central anode from the

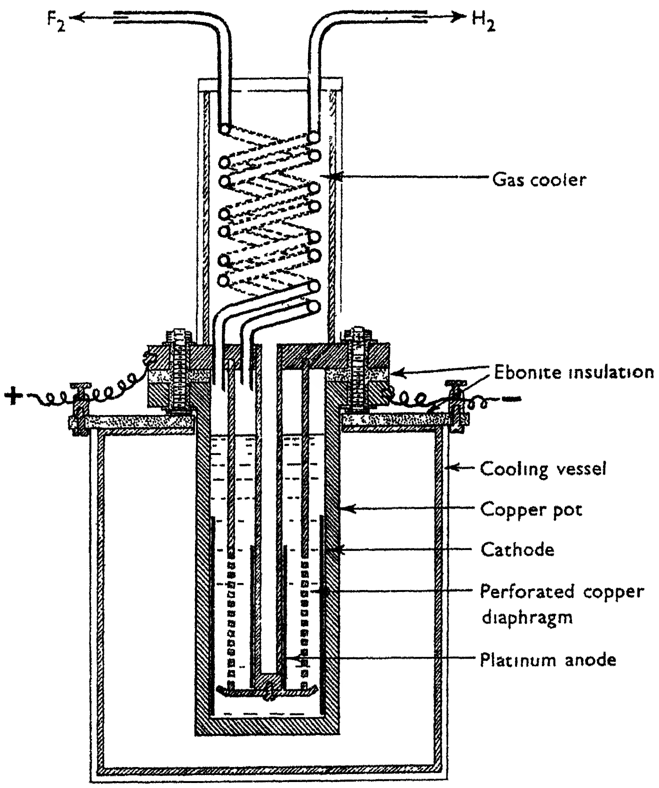

Fig. 1. FLUORINE CELL: POULENC FRERES & MESLANS

cathode. (Fig. 1). The diaphragm was itself a copper vessel, with perforations below the electrolyte level; it was at the same potential as the anode, but became covered with a non-conducting film of fluoride, so that it was insulated from the electrolyte and did not function as an anode. It was closed at the base, to prevent hydrogen entering the anode compartment from below, and the perforations gave access for electrolyte between anode and cathode compartment. There was no need to provide a non-conducting seal within the diaphragm, exposed to fluorine, for the current lead to the anode since the diaphragm could be sealed through the cell cover on the cathode side, exposed only to hydrogen and hydrogen fluoride. The walls of the copper pot served as cathode. This design of cell was used by Ruff in much of his fluorine work.[34] Cuthbertson and Prideaux[35] analysed the gas made by Moissan's method and found 50 – 60% fluorine, with varying proportions of oxygen and nitrogen in the remainder.

Mellor (II,9) was able to refer to the newer electrolytic process for fluorine first described by American workers in 1919. It was shown that molten Frémy's salt, KHF_2, could be electrolyzed in a copper vessel and with a graphite anode to give fluorine, and this method, associated with the names of Argo and Mathers, is so much cheaper and simpler and more convenient than Moissan's method that the latter was almost immediately completely superseded. In the following 25 years, more than 50 original articles and patents appeared on the production and use of fluorine; of the cells employed, two are related to Moissan's, 40 to Mathers' and 8 to a subsequent development associated with the names of Lebeau and Damiens. The arrangement of most of the cells described is based on that first proposed by Poulenc and Meslans. Cells based on the electrolyte introduced by Moissan are described as low temperature cells, whilst those using the new electrolyte composition of Argo and Mathers are called high temperature cells. Subsequently medium temperature cells appeared, based on an 'intermediate' electrolyte introduced by Lebeau and Damiens.

The studies by Mathers and his colleagues on the chemical production of fluorine and their development of an improved electrolytic process arose from chemical investigations fostered by requirements of the 1914–18 war. The 1939–45 war gave a further impetus to fluorine production, because it was needed for making uranium hexafluoride and fluorocarbons, so that large scale production was established.[36] It is convenient, therefore, to consider the development of fluorine production since 1919 in two stages, with the 1939–45 war as the dividing line. In the inter-war period there were two reports of cells of the low-temperature type. Brunner[37] in 1920 described a concentric cell, after the pattern of Poulenc and Meslans, with an axial platinum cylinder as anode, a surrounding copper diaphragm, and a copper pot as container and cathode; this pot was cooled in calcium chloride brine. The second, which worked in a region between low and medium temperature, is considered later[72] (see page 28).

HIGH TEMPERATURE CELLS

Artificial graphite of the Acheson type, the material used as anode in many electrolytic processes, disintegrates when made anodic in Moissan's electrolyte. It was Mathers' outstanding discovery that in fused potassium hydrogen fluoride graphite was practically unattacked and could be used as anode.[38] This electrolyte also had other advantages: the partial pressure of hydrogen fluoride over it is very much lower than with low temperature electrolyte, and the loss of hydrogen fluoride is therefore much reduced. The cell may be open on the cathode side, and operating with heating at 250°C. is more convenient than operating with cooling at -15° to -30°C (Fig 2). It is surprising that this discovery was not made earlier, and in

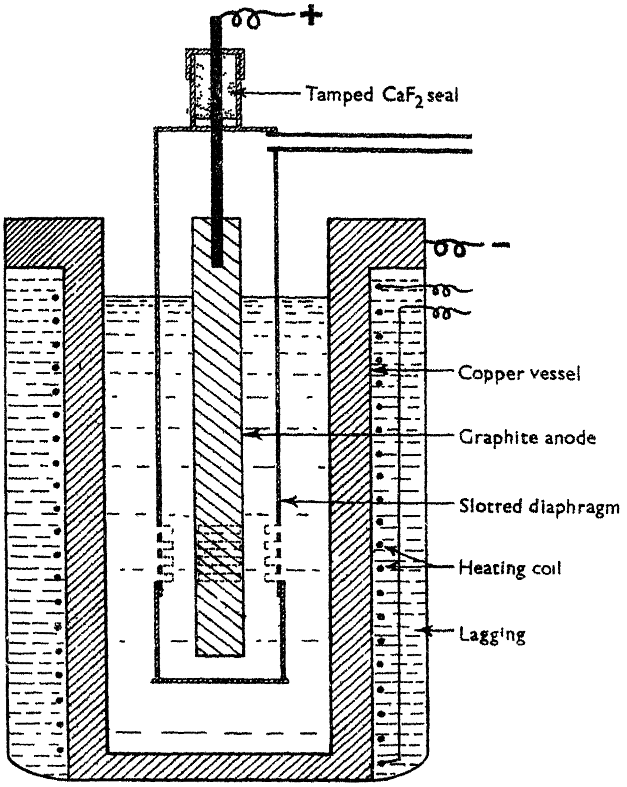

Fig. 2. FLUORINE CELL: ARGO, MATHERS ET AL.

particular that Ruff, in all the years covered by his work on fluorine, did not find this much easier way of making it. Ruff indeed said that the preparation of fluorine would always remain a difficult laboratory operation, owing largely to the trouble of making and handling anhydrous hydrogen fluoride. Mathers, on the other hand, considered that there were no special difficulties in the manipulation of the new apparatus.

Of the many cells based on Argo and Mathers' electrolyte[38-60] the majority had a concentric cylinder arrangement, although an eccentric arrangement in a cylindrical cell was also tried[55] and a V or U shape (reverting therefore to Moissan's original form) was introduced by Dennis, Veeder and Rochow[56] and was adopted by a number of other workers [57-60] (Fig. 3). The capacity of these cells was usually about 5 amp. and sometimes up to 15 amp., the largest mentioned having 30 amp. capacity.[54] The containers were usually of copper, as was the diaphragm, but it was generally agreed that copper suffered appreciable corrosion and the electrolyte became fouled with copper fluoride which could cause foaming.[38] It was found necessary to insulate the diaphragm from the anode, thus introducing the problem of an insulating, fluorine resistant, seal between these two parts, a

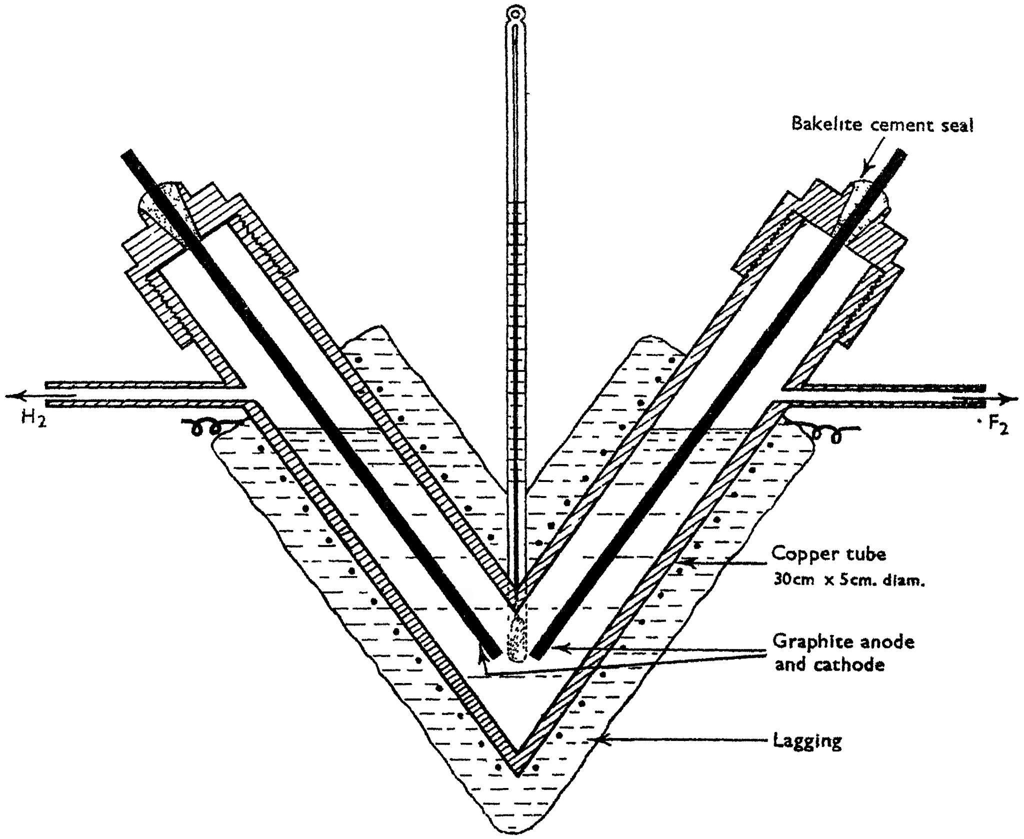

Fig. 3. FLUORINE CELL DENNIS, VEEDER & ROCHOW

problem which was solved in a number of ways. The copper diaphragm still tended to acquire an insoluble, insulating coating, which prevented its acting as a bipolar electrode and reduced its rate of corrosion. Argo and Mathers tried a graphite crucible, which was of the clay-bonded type, not of artificial graphite; they reported its failure owing to the presence of the clay binder. Another cell, of artificial graphite, has been described[40] but this has been criticized because solidification of the electrolyte causes breakage.[43] Containers made of magnesium,[44] magnesium – 2% manganese alloy,[55] nickel[43-58] and Monel[43, 46, 53] have all been tried, and with these the corrosion is usually reported to be very slight. Magnesium has also been used for the diaphragm.[44, 55] In the cylindrical cells the pot is usually the cathode, but cathodes have also been tried of silver sheet[55] and, in the V-shaped cells, of graphite. The anodes were always artificial graphite, but occasionally of a special specification. It will be seen below that disturbances – increase in voltage and reduction in current – were liable to occur in operation; this was sometimes attributed to the deposition of silicon present in the electrolyte or in the anode, and low silicon or spectrographically pure graphite was specified.[43, 56, 60] No explanation was offered as to how such a deposition could occur. In the arrangement of the cell, the anode and other connections were usually through the top, and in the cylindrical cells they would be on the diaphragm bell, which rested often in an open bath of electrolyte. The insulation of the diaphragm from the anode connection passing through it caused a good deal of trouble; a powder of calcium fluoride was tamped in[38] or a compressed ring of the same material was used,[39, 40, 48] with assistance from red lead–glycerol cement,[40] or calcium fluoride–asbestos,[48] the simple solution of Portland cement, introduced by Simons[43] was often used[44, 46, 49, 59] sometimes assisted by molten electrolyte poured over and allowed to solidify.[59] A cement of calcium fluoride and sodium silicate was also used[52, 56, 58] or a bakelite cement.[56] A glass and rubber sleeve arrangement, sealed by the products of attack on the rubber was another simple solution,[57] and the use of a pressure union was a very practical device.[60] Another early, practical solution was the use of a motor car sparking plug.[39] The graphite anode might pass through the seal and electrical connection be made to it outside the cell, or a threaded hole might be made in the graphite, to which a copper[40, 44, 46, 59] or nickel[58] rod could be fitted. In one cell the problem was solved in another way; the anode, entering through the base of the cell, was sealed by solidified electrolyte in a long air-cooled sleeve.[55] The cylindrical cells were usually about 3 in. diameter, and 9 in. long, holding up to 3·5 kg. of electrolyte: they were externally wound with resistance wire for electrical heating, and lagged.

The V-shaped cells were usually made of 2 in. copper pipe, 12 in. long in each leg. The graphite anodes were usually 1 in. cylindrical rods (occasionally 0·5 in.) and up to 12 in. long: in one case the working end of the anode was wider than the part above and slotted, to give a lower current density.[40]

The fluorine was usually withdrawn by a side arm on the diaphragm bell, and the desirability of having a wide side arm to avoid blockage by electrolyte spray was frequently stressed. In one case a settling chamber was attached to the side arm, to aid the deposition of electrolyte carried in the fluorine stream.[56] In another case the fluorine outlet was through a hollow copper tube which also served as anode connection.[48] The electrolyte was usually potassium hydrogen fluoride, frequently specified as Kahlbaum's or Merck's purest. The commercial availability of this salt made the preparation easier than it had been for Moissan and earlier workers, who had to make their own salt.

A very high resistance was found on first starting the cell, and the current-voltage relation was very erratic. At first it was usual to electrolyze for some time at low current density, or to apply a very high voltage, up to 110 volts D.C., for a short period. Sometimes a pre-electrolysis was preferred outside the fluorine cell.[43, 49] This polarization effect was due to the presence of small amounts of water, as was shown in the work of Fredenhagen and Krefft considered below, and long-continued drying at about 150° was used after 1930, to give an electrolyte which produced fluorine immediately. At 150° the loss of hydrogen fluoride from the salt during drying was very slight.

Some variants on the straightforward high temperature electrolyte have been investigated. The use of the sodium salt, $NaHF_2$, alone is not possible, because it decomposes without melting, but amounts up to 35% have been added to the potassium salt, when the cell will work at 170°, and there is less creep of the electrolyte and less tendency to polarization: there is, however, a greater amount of hydrogen fluoride in the gases produced, so that this addition is not advantageous.[44] Other additions, such as lead and strontium fluorides, were no better.[40] An electrolyte to work at lower temperature was proposed by Lebeau and Damiens (see below). Mathers and Stroup had earlier considered this possibility, but their work was not published until a good deal later.[61] They considered double fluorides of the

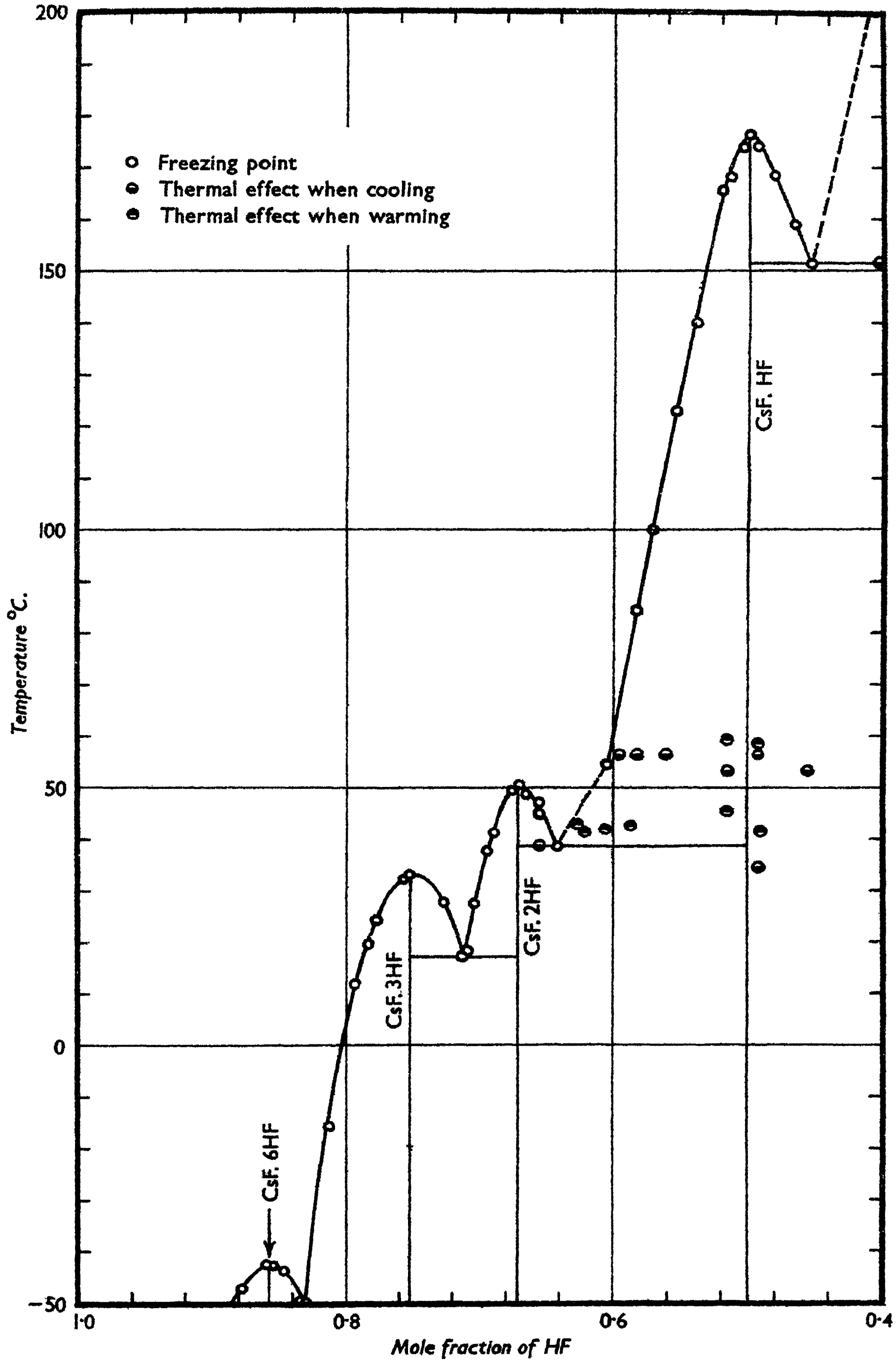

Fig. 4. FREEZING POINTS IN THE CsF - HF SYSTEM

type of K_2SnF_6; the derivatives of tellurium, titanium, manganese, lead and tin, all had higher melting points than potassium hydrogen fluoride, and potassium hexafluoroantimonate, $KSbF_6$, which had a melting point above 300°C., gave no fluorine on electrolysis, but thick white fumes and severe anode corrosion. Lithium hydrogen fluoride, like the sodium salt, decomposes on heating without melting.

The caesium fluoride–hydrogen fluoride system was, however, of interest and attention was drawn to the appreciably lower melting points in this system. Subsequently some of the salts in the rubidium fluoride system have been studied, and the following table has been given[85]

TABLE I – MELTING POINTS OF ACID FLUORIDES

Alkali metal	Melting points (°C.) of salts with:-				
	1 HF	2 HF	2·5 HF	3 HF	4 HF
Potassium	239	71·9	64·0	65·8	72·0
Rubidium	210	62·5	–	52·0	32·0
Caesium	169	48·0	–	33·0	below 0°

Somewhat different figures have been given by other workers:

	1 HF	1·5 HF	2 HF	3 HF	6 HF
Rubidium[63]	204–205	–	51·6	0°	–
Caesium[61]	142	30	–	–	–
Caesium[64]	176	–	50·2	32·6	–42·3

Mathers and Stroup carried out electrolyses in a small magnesium cell using a caesium fluoride electrolyte melting below 19°C., and with a graphite anode. It is found, as would be expected, that owing to the generally lower melting points in the caesium fluoride system, the losses of hydrogen fluoride in the electrolytic products are very much reduced, and it seemed that there would be some advantage in working with a caesium fluoride electrolyte, instead of potassium fluoride, if the caesium salts were less rare and expensive. The caesium fluoride–hydrogen fluoride system has been investigated in more detail,[64] and is shown in Fig. 4. Fig. 5 gives the data of Cady for the potassium fluoride–hydrogen fluoride system, and Fig. 6 gives his data for the partial pressure of hydrogen fluoride.[62] The pronounced minima in these partial pressures shown by the salts KF.HF and KF.2HF indicate the value of these electrolyte compositions from the standpoint of hydrogen fluoride losses.

The cells using the high temperature electrolyte, KF.HF, were operated at a temperature a little above the melting point, initially about 250°C. But as electrolysis proceeded and the hydrogen fluoride content diminished, the melting point and the operating temperature rose, the electrolyte was discarded when the temperature reached 280°.[52, 58] Before this occurred the voltage increased appreciably, and on occasions complete polarization occurred, with no current passing at much higher voltages across the cell. This effect was different in character from the starting up effects due to traces of water, which were clarified by Fredenhagen and Krefft. A cell which initially worked at 9 v. would in time require 14 v. for the same current,[50] and when the anode was too old, practically no current passed even at 60 – 90 v.[50] In another case, it was suggested that the cell worked well below a certain limiting current density, above which, however, polarization suddenly occurred.[55] This effect was connected with the development of a glossy surface on the graphite anode, which was said to contain

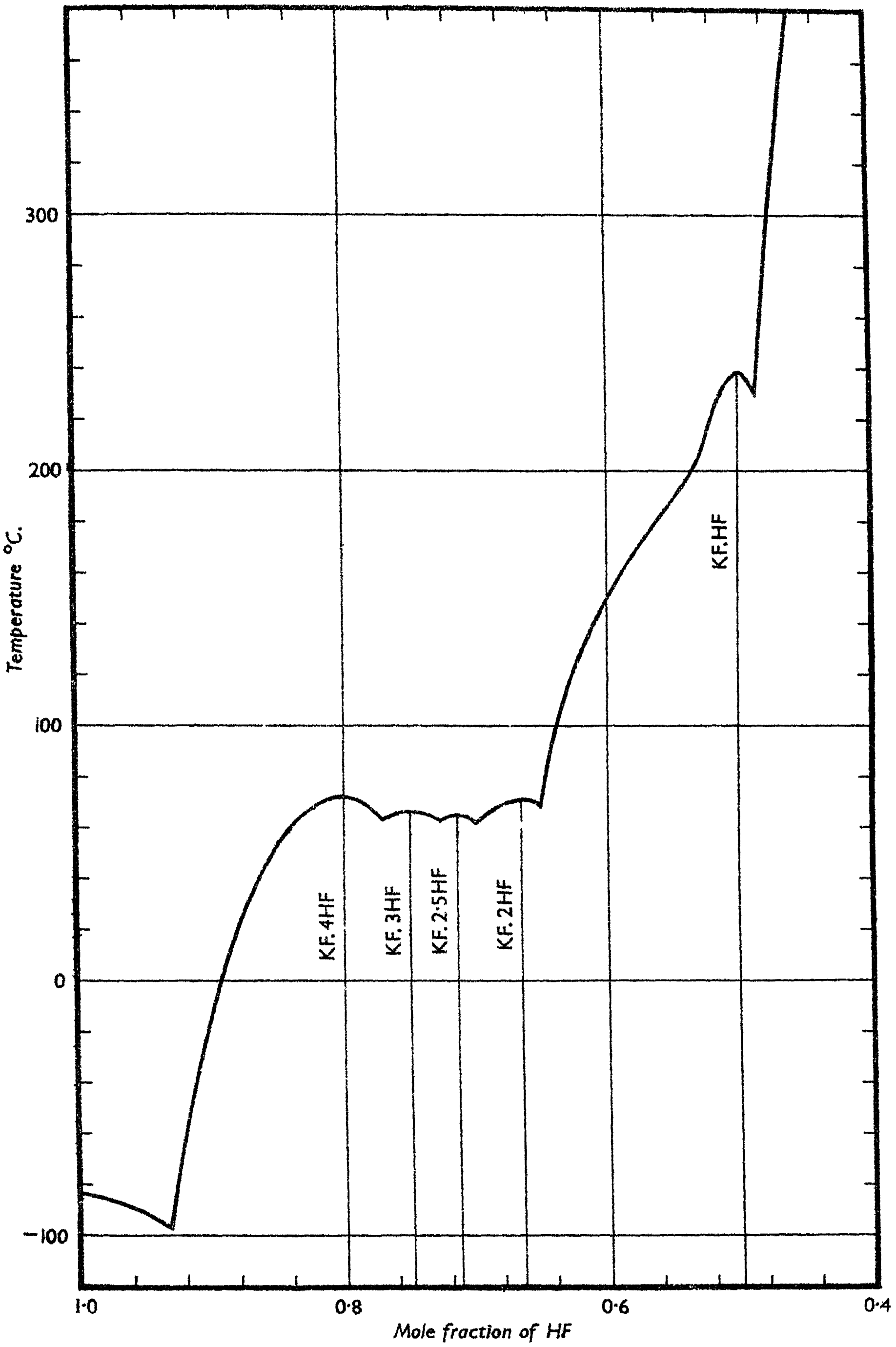

Fig. 5. FREEZING POINTS IN THE KF-HF SYSTEM

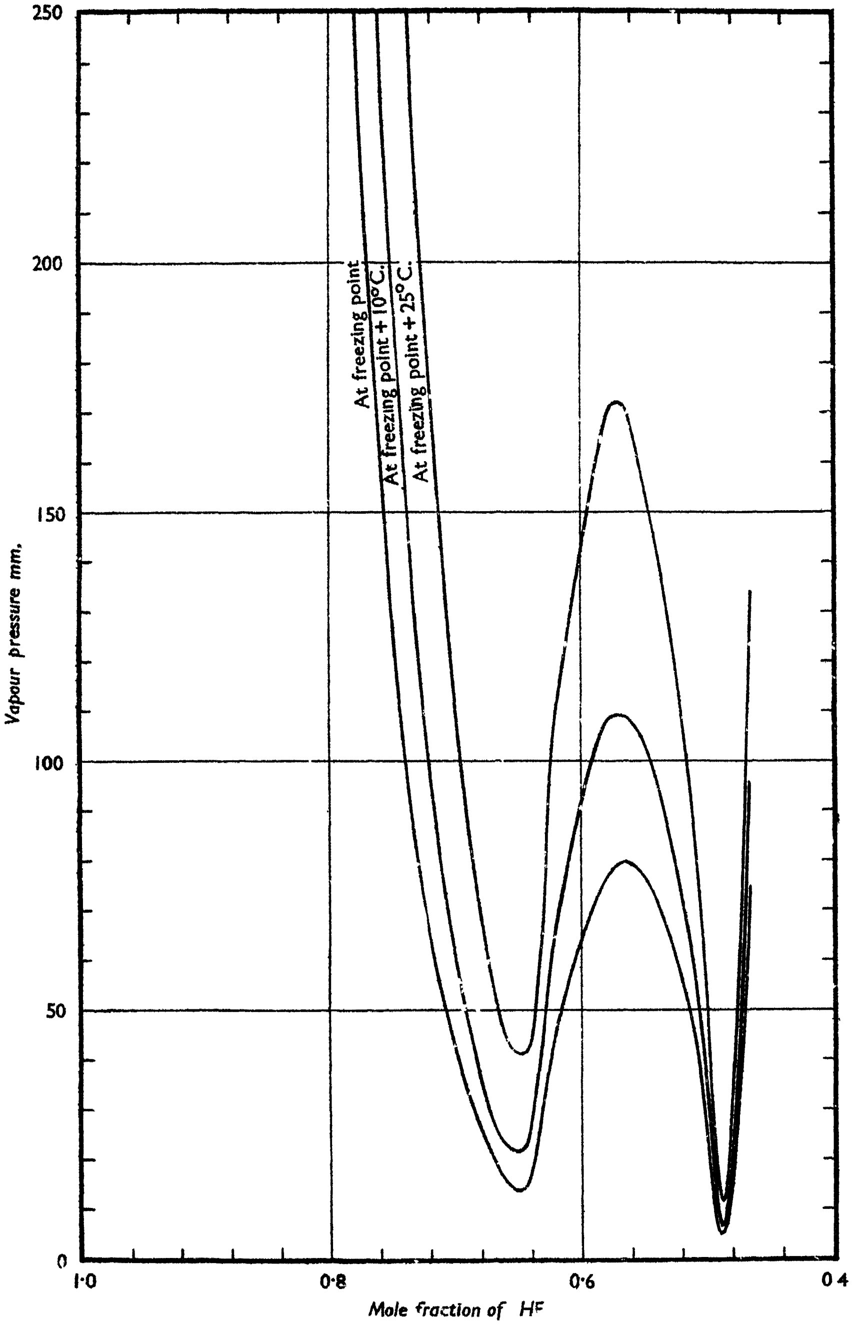

Fig. 6. PARTIAL PRESSURE OF HF OVER THE KF-HF SYSTEM

silicon.[56] When electrolysis was interrupted by this glossy coat, the anode should be removed, and the surface sand papered, when the anode would perform satisfactorily again.[60] The true cause of this effect was discovered much later (see page 40).

The current efficiency of the cells has been variously given as between 30% and 90%. In one case, in a V-shaped cell, the efficiency (determined by displacement of iodine from potassium iodide, or of oxygen from water) rose from 45% at 5 amp. to 76% at 9 amp.[56] In another cell of this type, the current efficiency at 5 amp. fell from about 90% at the start, to 60% when the electrolyte was ready for discarding. More generally, the efficiency is given as 70 – 80%,[40] 80 ± 5%,[43] 70 – 85%,[50] 80%,[52] 75%.[55]

The fluorine given by these cells is contaminated with 5 – 10% (by volume) of hydrogen fluoride, which was quite generally removed by passage through sodium fluoride. (For purification, see page 42). Although Cuthbertson and Prideaux, as we have already seen, determined the fluorine content of their product, but few analyses were made until in 1936 the gas from a U-cell was analysed by shaking with mercury: the fluorine content was found to be 97 – 99%, with carbon dioxide 0·2 – 1·3%, oxygen 0·4 – 1·6%, and inerts (carbon tetrafluoride and others), 0·3 to 0·4%.[58] About the same time a V-cell gas, analysed by the same method, was reported as containing 97% after 5 hours operation, and after 20 hours, 99·8% of fluorine, with small amounts of carbon tetrafluoride, ozone, chlorine, etc.[59] Suggestions regarding the presence of small amounts of carbon tetrafluoride in the gas were frequently made but positive proof of this is lacking. In one case it was concluded that there was not more than 0·2% of carbon tetrafluoride,[40] in another case it was recommended that the gases should be cooled with old liquid air, when not only carbon tetrafluoride, but higher homologues still liquid above 0°C., were condensed out.[53] Again, it has been suggested that from the rate of anode wear, the carbon tetrafluoride content could not exceed 3%.[53] Lebeau and Damiens, who first corrected Moissan's quite erroneous characterization of carbon tetrafluoride from their identification of it in the anodic gases in the electrolysis of molten beryllium fluoride, were thus led to identify it in the anode gases from the high temperature fluorine cell.[75] They found the proportion of carbon tetrafluoride increases with the temperature, with the anodic current density, and with the voltage. At over 40 volts, no fluorine was evolved, and this was said to be a good way to make mixtures rich in carbon tetrafluoride. It was this observation which caused them to seek an electrolyte which could be used at a lower temperature. Later workers also remarked that at temperatures above 300°C. graphite anodes are severely attacked.[78]

Considering individual cells, detailed accounts are given of the design and operation of cells of this type in 15 cases.[38, 40, 41, 43, 44, 46, 48, 50, 52, 55 – 60] The cell described by Simons in 1924[43] was frequently copied; it was based on not very considerable modifications of the Argo and Mathers design. The most unusual cell was that described by Bodenstein, Jokusch and Krekeler, with a cast magnesium body, bottom-entry electrodes air cooled, a slotted magnesium diaphragm and perforated silver cathode.[55] (Fig.7.) Certain features of this cell were the subject of patent claims by I. G. Farbenindustrie, and also seem to have been the basis of wartime expansion, but not by I. G. Farbenindustrie.

The V-shaped cell, introduced by Dennis, Veeder and Rochow,[56] representing a return to Moissan, was also copied. It was usually made from copper pipes brazed or welded together, but Miller and Bigelow had a very heavy cast nickel U-shaped cell of this type.[58] A number of cells, or cell features, have been the subjects of patents. That of Poulenc and Meslans has already been referred to.[33] The claim here was for an anodically connected partition between anode and cathode, made of metal such as copper,

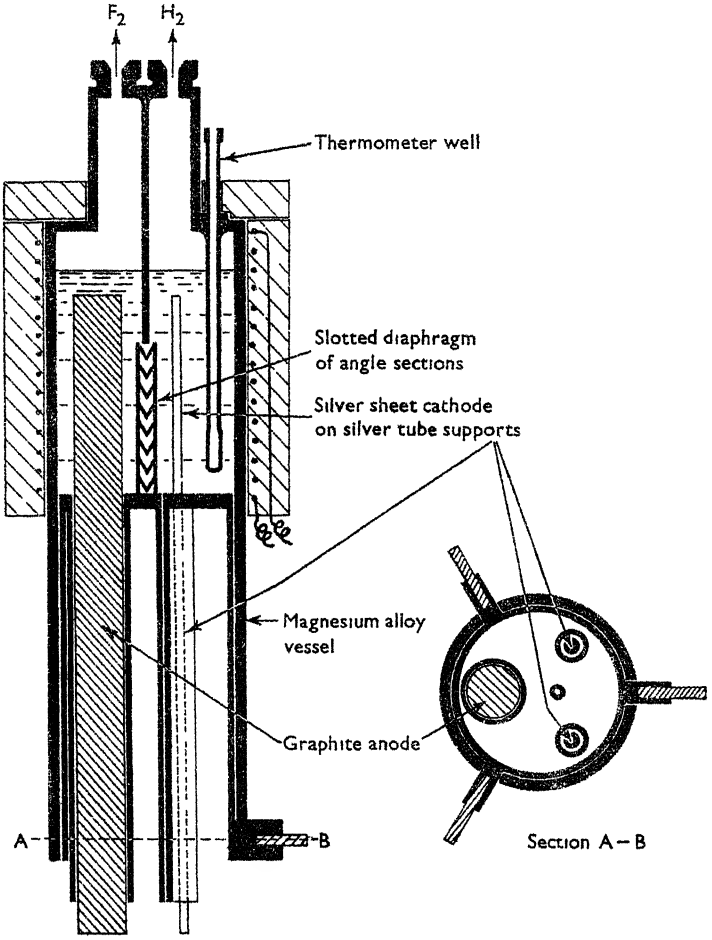
F₂
H₂
Thermometer well
Slotted diaphragm of angle sections
Silver sheet cathode on silver tube supports
Magnesium alloy vessel
Graphite anode
A
B
Section A – B

Fig. 7. FLUORINE CELL: BODENSTEIN, JOCKUSCH & KREKELER

which by holes below the electrolyte level served as a diaphragm. Mathers claimed the electrolysis of a fused acid fluoride with an anode of hard carbonaceous material[65] and, with Humiston, a cell for this operation, with various features including a graphite vessel.[66] Lebeau and Damiens claimed the use of an electrolyte of hydrofluorides of m.p. between 0° and 150°, with an anode of a common metal, iron, nickel, etc., with an anodic diaphragm.[67] Fredenhagen claimed carbon or graphite anodes in a melt not wetted by the electrolyte, about KF,1·7HF[68] and a method of drying the electrolyte and testing for dryness.[69] Krekeler claimed the solid electrolyte as jointing and insulating material for the electrode leads, and electrodes entering from below, from the side, or from above.[70] Another patent claimed the use of fluorine for drying the electrolyte[71] and again the use of nickel anodes in electrolyte of hydrogen fluoride with 30–50% of potassium hydrogen fluoride, at temperatures of 30–35°C., was the subject of a patent of American origin.[72] Perhaps the judgment on this is contained in a later paper to which one of the inventors was a contributor: 'After preliminary tests

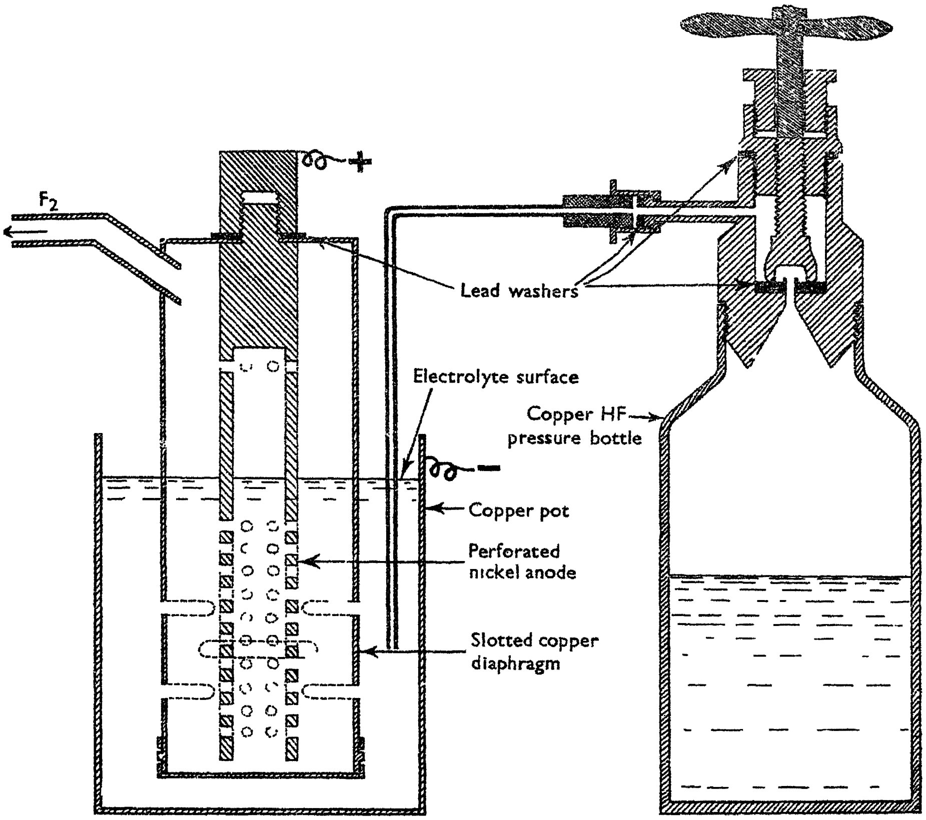

Fig. 8. FLUORINE CELL WITH PROVISION FOR BATH REGENERATION: LEBEAU & DAMIENS

indicated that the corrosion would be severe at room temperature because of the higher acidity, further work was confined to medium temperature conditions'.[89] The treatment and use of rubber[73] and rubber-like materials[74] in fluorine cells has also been claimed.

MEDIUM TEMPERATURE CELLS.

Lebeau and Damiens, because of the work on fluorine purity referred to above, proposed a salt with a higher content of hydrogen fluoride, KF.3HF, m.p. 56°C., to be used below 150°C., and an anode of iron or nickel, preferably the latter because of its freedom from carbon.[75] Excessive claims were made for the current efficiency, which was said to be as high as 96–97% at 60–70°C., falling to 30% at 160°. Later work has shown that the efficiency with a nickel anode in this electrolyte is only of the order of 70%, and that heavy corrosion of the nickel occurs. Nevertheless this work did open a new avenue, which has developed into the preferred route to fluorine. These workers also collected liquid hydrogen fluoride in a steel bottle, having made it by heating Frémy's salt, and at intervals evaporated it into the cell to renew the electrolyte. (Fig.8.)

Fredenhagen and Krefft[76] showed that the abnormal phenomena on starting a high temperature cell could be related to the water content. The production of anhydrous hydrogen fluoride of very low water content was worked

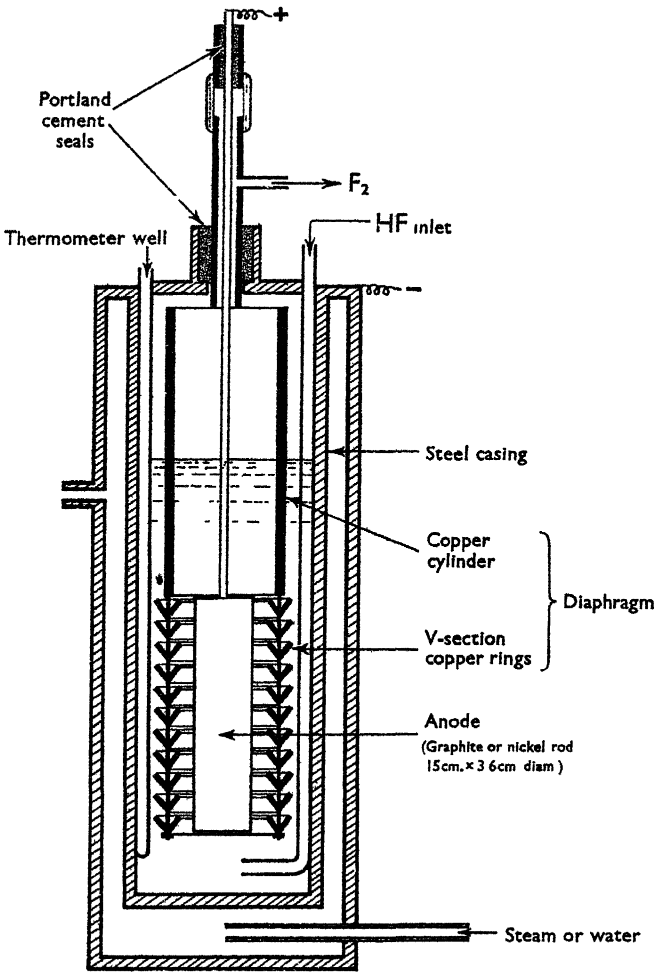
+
Portland cement seals
F_2
Thermometer well
HF inlet
−
Steel casing
Copper cylinder
Diaphragm
V-section copper rings
Anode
(Graphite or nickel rod 15cm.× 3 6cm diam)
Steam or water

Fig. 9. FLUORINE CELL: CADY, ROGERS & CARLSON

out by Fredenhagen and Cadenbach,[77] and this was used for electrolyte renewal. It was found that the electrolyte rapidly absorbed hydrogen fluoride, and it was convenient to continue until an electrolyte composition of about KF,1·6HF was reached, when electrolysis could be started at 160°C., with a graphite anode. With hydrogen fluoride contents below KF,1·8HF, the electrolyte did not wet graphite, and graphite anodes could be employed, but above this proportion of hydrogen fluoride wetting took place and graphite anodes were destroyed. This was made the subject of a patent.[68]

It was suggested by Henne that, starting with molten Frémy's salt, hydrogen fluoride could be added to attain a composition corresponding to KF,3HF, and that graphite anodes could be used in this electrolyte.[60] Later work failed to confirm this. Cady, Rogers and Carlson used an electrolyte of composition about KF,2HF, and stated that up to KF,1·85HF graphite anodes stand up well, though at higher hydrogen fluoride concentrations they

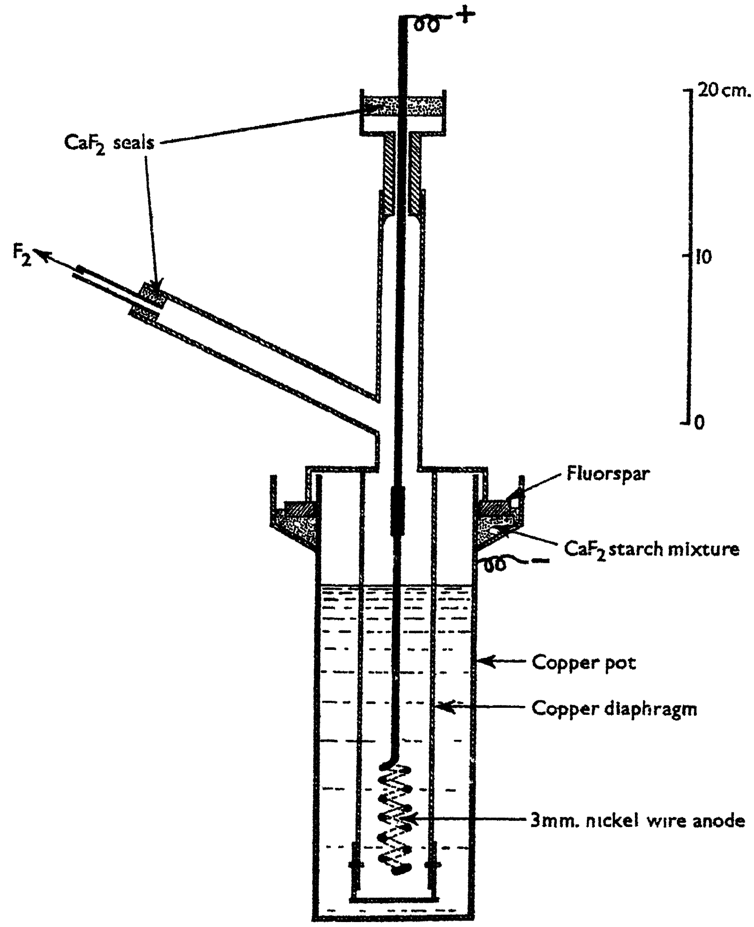

Fig. 10. FLUORINE CELL: VON WARTENBERG & KLINKOTT

disintegrate.[78] It was shown that the explanation of this effect as due to the wetting of the graphite by the electrolyte could not be true, because in a cell where graphite as anode was not wetted and not disintegrated, a graphite cathode was wetted but yet not disintegrated. The non-wetting effect persists; e.g. if a non-wetted anode is held under the tap, it is unwetted by tap water. These workers also showed that a mild steel pot was satisfactory for medium temperature cells.

Lebeau and Damiens returned to the expedient of Poulenc and Meslans of having the diaphragm anodic, and this was used also by Cady, who had a nickel sheet cylindrical anode resting on the base of the diaphragm and leading the current to it [79] (Fig. 9). It has been seen that Fredenhagen and Krefft claimed to be able to use graphite in electrolyte of composition KF,1·6HF. Von Wartenberg and Klinkott worked at about KF,2HF, and used a coiled nickel wire as anode, which could be uncoiled as the end of the wire was corroded away.[80] (Fig. 10) A similar cell was used by other workers at KF,3HF.[81] Tian made a critical comparison of the cells of

Lebeau and Damiens, and of Dennis *et al.*, and rather favoured the latter.[57] Cady was the first to report the use of commercial anhydrous hydrogen fluoride for electrolyte make-up.[79]

WARTIME AND POST WAR DEVELOPMENT OF FLUORINE PRODUCTION

A good deal of knowledge on the problems arising in the production of fluorine had accumulated when wartime requirements, especially in the U.S.A. and Germany, called for large quantities of the element but many of these problems were still unsolved and there was indeed no agreement as to which range of electrolyte, medium temperature or high temperature, was to be preferred. It will be shown below that in the U.S.A. the principal development was of medium temperature cells, at first with nickel anodes, later with amorphous carbon anodes, though there was one promising high temperature installation. In Germany, on the other hand, there was a large manufacturing plant using high temperature cells, and one promising large scale medium temperature cell. Discussion of the relative merits of the two types of cell must cover a number of points.

As to the precise electrolyte composition (or range of composition), its regeneration, and the control required, there is probably little to choose between the types, and as to hydrogen fluoride consumption, provided that the medium temperature cell is operated nearer the KF,2HF of later workers than the KF,3HF of the original proposers, the proportion of hydrogen fluoride in the fluorine is about the same in both cases (Fig. 6). Concerning fluorine purity, however, there should be a complete absence of fluorocarbons from the medium temperature cell product, and its oxygen content will depend entirely on the water content of the hydrogen fluoride supply. In materials of construction, the medium temperature cell has a very definite advantage if (as was later confirmed) steel can largely be used in its construction, whereas in the high temperature cell copper is definitely corroded and there may be a need to use more expensive materials, like nickel or magnesium or their alloys. For anodes, graphite will be used in the high temperature cell, but its tendency to gradual polarization, calling for some remedial action, will complicate operating procedure. The anode for the medium temperature cell is the biggest problem: if nickel is necessary, the reduction in current efficiency, the usage of nickel, the accumulation in the cell of insoluble nickel fluorides, and the need to treat the electrolyte to remove this sludge, would probably throw the balance in favour of the high temperature cell. If carbon or graphite anodes could be used, the balance would certainly be in favour of the medium temperature cell.

It was found in fact that graphite was not satisfactory in the range of electrolyte composition preferred for the medium temperature cell; but that amorphous carbon, i.e. hard carbon of the arc lamp or furnace carbon type, was satisfactory, although it still showed polarization in a somewhat erratic and unpredictable manner. The medium temperature cell was used on a considerable scale in the U.S.A. during the war, at first with nickel anodes, but later with carbon anodes, and the different users, there and in Germany, put forward a variety of proposals for controlling polarization. These will be considered after a general account has been given of the different cells which have been described.

The American wartime developments in fluorine cells were described in 1946 at a fluorine symposium[36] and published in 1947.[82] Fuller accounts of some of the wartime work have more recently appeared.[83] These were mostly developments sponsored by the U.S. Atomic Energy Commission, and since these relatively early experiences no further information has been released on fluorine production in this field. A foreign estimate suggests

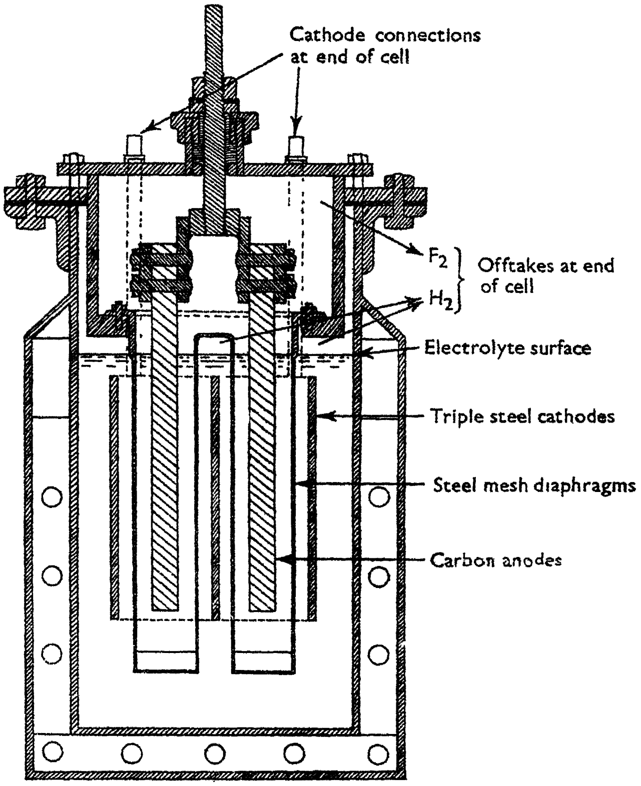

Fig. 11. 1000 AMP. FLUORINE CELL HOOKER

that American production capacity is 5000 – 15,000 tons per year.[98] The developments in German fluorine production are largely described by Allied investigating officers immediately after the war.[84–6]

Three large American medium temperature fluorine cells, produced by the Hooker Electrochemical Company,[87] (Fig. 11) the Harshaw Chemical Company[88] and the Du Pont Company[89] have been described. They were generally of steel construction, of long rectangular shape, e.g. the Du Pont cell was 4 ft. × $1\frac{1}{3}$ ft. × $2\frac{3}{4}$ ft. deep, jacketed for steam or water heating when off load, and of 1000 – 2000 amp. capacity. The anodes were carbon, although the Du Pont cells were first started with nickel anodes. A good deal of information has been given on the operation of these large cells with nickel anodes.[83,90] Graphite as anode was found to swell and disintegrate; e.g. a graphite anode in a stream of fluorine gained 6% in weight after 26 hours at 100°C., and increased in size, whilst a hard carbon anode gained only 0·28% in weight and showed no dimensional change.[88] Steel sheet cathodes were used, and the anodes were separated from them by diaphragms either of 6 mesh steel screen on a steel frame, which would last a year or longer[87] or of 8 mesh Monel metal screen;[88,89] care had to be taken in the design and construction of these diaphragms to prevent corrosion occurring owing to bipolar electrode effects. The method of connection to the anode varied, and the Hooker workers were of the opinion that this connexion is the biggest problem in fluorine cell design. They found the best connexion was by copper plates bolted on to the flat carbon anodes, 18 in. × 6¼ in. × 1¼ in., with copper bolts, with a special carbon electrode paste between the copper and the carbon. Du Pont used a similar connexion, but Harshaw had 1¼ in. diameter carbon rods, 12 in. long, into which a copper rod was forced, with a steel or copper circumferential band fitted. In all these cells the anodes were insulated from the cover by means of the recently discovered polytetrafluoroethylene of Du Pont ('Teflon'). The anode-supporting leads passed through a stuffing box and rings of 'Teflon' were placed over them, the upper and lower rings having a filling of calcium fluoride to give rigidity. Various connexions were provided on the cell cover; for adding hydrogen fluoride, for sampling electrolyte, for sweeping out with nitrogen, as well as, of course, for removal of fluorine and hydrogen.

The cells operated with electrolyte containing 37 to 40% hydrogen fluoride, at temperatures between 95° and 115°, and preferably about 105°C. Hydrogen fluoride was added at intervals of four hours. The current density was about 75 amp. per sq.ft. on full load, the voltage in normal operation, at the start, would be 8 – 9 volts, and the current efficiency on fluorine is variously given as about 90%[89] and close to 95%.[88] The fluorine is said to contain between 4 and 8% of hydrogen fluoride with an average of 6%,[87] and 5 – 15% of hydrogen fluoride.[89] Obviously, the exact amount will depend to some extent on the electrolyte composition, but, in the narrow range of compositions used, principally on the temperature. After removal of the hydrogen fluoride, the following analyses are recorded:-

	Per cent.[87]	Per cent.[89]
Fluorine	99·0 – 99·4	98
Carbon dioxide	0·12 – 0·14	–
Oxygen	0·3 – 0·5	*ca.* 1
Nitrogen and inert gases	0·1 – 0·4	*ca.* 1
Fluorine oxide	–	small amount

Among troubles with these cells, corrosion was unimportant if care were taken in the design and construction of the diaphragm. The principal trouble was polarization, which could arise from a number of causes including the composition of the electrolyte, failure of the anode connexion, and the peculiarities of the carbon anode. As to the electrolyte, water could cause trouble, particularly on starting a new cell; in the manner usual with high temperature cells, a high resistance developed and the cell current dropped. This was overcome by starting a cell on a nickel anode, which did not show any effect due to water; hence all the cells incorporated a subsidiary nickel anode. If the hydrogen fluoride content fell below about 37·5%, some polarization occurred, but this was easily rectified by adding hydrogen fluoride. The contact between the anode carbon and the copper connexion tended to deteriorate, and this led to a gradual increase in voltage.[89] If the contact failed completely on one anode plate an excessive load would be thrown on the other plates in the cell, and polarization was very common when an anode was operated at a high current density for any length of time. The only cure for this defect was to take the cell off load and replace the anode block. An anode life of about three months was found in one case [87] Finally there was polarization due to less obvious causes. The Harshaw workers attribute it to non-wetting of the carbon anodes, and describe how lithium fluoride, which was added in an attempt to reduce the hydrogen

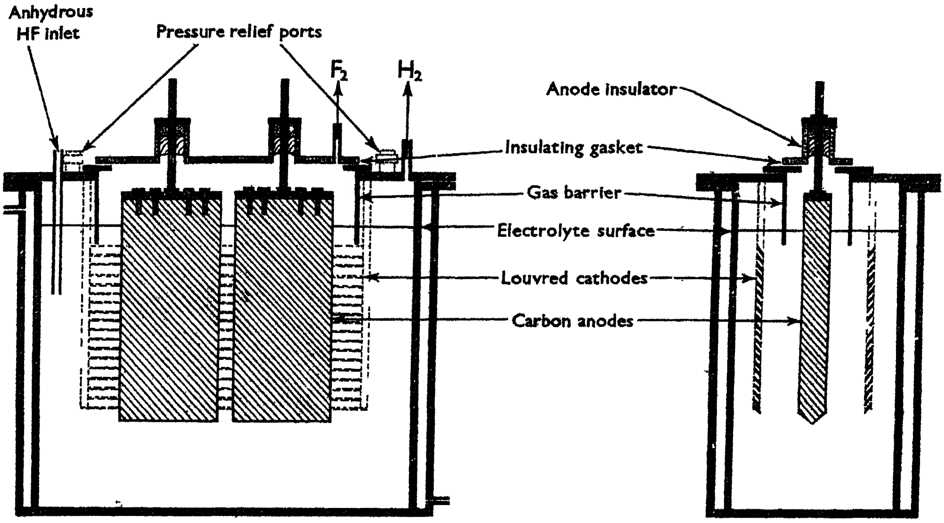

Fig. 12. 250 AMP. FLUORINE CELL: PENNSYLVANIA SALT MANUFACTURING CO.

fluoride loss, seemed to improve the wetting of the anode by the electrolyte. Further study showed that aluminium fluoride and sodium fluoride were effective, but 'since lithium fluoride was less readily precipitated from the electrolyte by reaction with contaminants than the other two', it became the standard addition. Quantities from 0·2% lithium fluoride up to saturation were all effective; normally 1·0 – 1·5% was used.[88] In a study of certain features of laboratory cell operation, however, Schumb, Young and Radimer[91] found that the concentration of added lithium fluoride diminishes with time, and finally reaches a small value when its beneficial effects disappear. Stirring up the sludge at the bottom of a cell in which this has occurred causes a temporary improvement. Analysis of three samples of electrolyte from Harshaw cells – one fresh, one used for a short period, one long in use – indicated a progressive reduction of the lithium fluoride content from 1·5% to 0·2%. Aluminium fluoride is also said to be only very slightly soluble in electrolyte. The exact effect, and the mode of action, of these additions is therefore obscure, and doubt has been cast on the suggestion that they cause wetting of the anode.[108]

Special types of amorphous carbon have been specified, to reduce polarization troubles. The Harshaw anode was impregnated with copper, which was found to give it greater strength, facilitated electrical connexion, and reduced the influence of the hydrogen fluoride content of the electrolyte. The anodes in the Du Pont cell were strengthened by impregnating them with carbonaceous material and rebaking. Reference has already been made to the use of auxiliary nickel anodes at the start of a cell, to eliminate water. With the Du Pont cell it was customary to switch to the nickel anode for a short period when polarization was serious.

Some operating data for smaller cells have also been given. The Harshaw Company describe a laboratory cell taking 50 amp., based on a single rod of their copper-impregnated carbon, and with the old concentric cylindrical arrangement of anode, diaphragm, cathode. Schumb *et al.*[91] give data on the distribution of voltage drop in a laboratory cell, and on the variation of specific conductivity, and specific gravity of electrolyte with hydrogen fluoride content. The chief interest of their cell, however, lies in the absence of any diaphragm between anode and cathode: there was a solid cylinder in the gas space, separating the gases arising from the anode and the cathode, and dipping into the electrolyte to provide a seal, but there was no screen of any sort below this. This was effective 'because of the close streamlining of the fluorine liberated at the anode, which prevented mixing of the gas with hydrogen from the cathode.' This is a considerable simplification in design. Both anode and cathode were insulated in passing through the cover, so that the sealing bell was at a voltage intermediate between them, as was usual in all the cells described in this section. A carefully designed cell of rather larger capacity, 250 amp., is also described.[92] This, the Pennsylvania Salt Manufacturing Co. cell, also had no diaphragm, only a sealing bell (Fig. 12). Another cell, of 15 amp. capacity, was a medium temperature cell of pre-war pattern;[93] and another of 25 amp. capacity, had a graphite anode, was generally of nickel construction, had no diaphragm between anode and cathode, and operated with an electrolyte containing up to about 1·8 moles of hydrogen fluoride per mole of potassium fluoride, specifically referred back to Fredenhagen and Krefft.[94]

I. G. Farbenindustrie designed a cell of 250 amp. capacity, first operated in 1940, and then a 2000 amp. cell which was started in 1942.[84-86] The cell body (Fig. 13) was made in cast magnesium alloy, 300 cm. long, 30 cm. square internally, having a 10 cm. external magnesium pipe for circulating electrolyte from end to end of the cell, with an internal water cooling pipe of nickel, and a cover of magnesium alloy sheet, with various connexions and apertures. The cathodes were magnesium alloy plates, on either side of the anodes, so that three rows ran the length of the cell. The anodes were made of specially hard carbon; amorphous carbon anodes were impregnated with pitch and rebaked at 1000°C., and the product was tested for breaking strength and hardness. The anodes were 35 cm. × 12 cm. × 5 cm., and 15 were arranged in line. For connexion, a copper rod was screwed into a tapped hole in the carbon. A sintered alumina bush resting on a shoulder on the copper rod fitted in the aperture in the cover and prevented access of fluorine to an outer bush of rubber which made a gas tight joint. The cathode leads were similarly insulated from the cover. There are no diaphragms in this cell but magnesium ribs project from the cover into the electrolyte and separate the anode and cathode gases. There are two end compartments separated by magnesium baffles from the electrolysis section: one has the hydrogen fluoride feed pipe and the electrolyte outlet connexion with an impeller causing circulation, the other has the electrolyte return connexion and an additional water cooling coil of nickel pipe.

The I. G. cell uses electrolyte of composition approximately KF,2·5HF, i.e. about 46% hydrogen fluoride, which is noticeably higher than in the American cells, and the working temperature, normally 75–85°C., is lower, as may be expected from the m.p. of such electrolytes. (Fig. 5) The anodic current density, 90 amp. per sq.ft., is rather higher than in American practice, the voltage is 11–13, and the current efficiency is said to be 85%. The

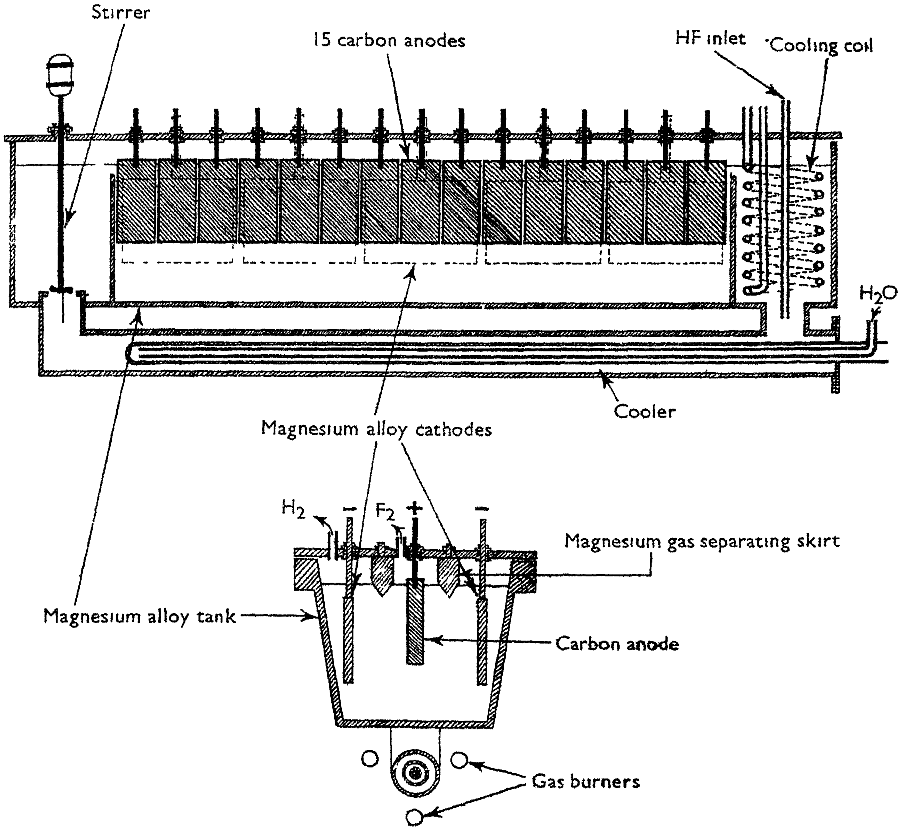
Stirrer
15 carbon anodes
HF inlet
Cooling coil
H_2O
Cooler
Magnesium alloy cathodes
H_2
−
F_2
+
−
Magnesium gas separating skirt
Magnesium alloy tank
Carbon anode
Gas burners

Fig. 13. 2000 AMP. FLUORINE CELL.I. G. FARBENINDUSTRIE

anhydrous hydrogen fluoride used was described as 'technical grade', with 96·5% HF, 2–3% of water, and up to 1% of hydrofluosilicic acid. This must be of much poorer quality than the American, judging by the oxygen content quoted for the fluorine from the latter, so it is remarkable that polarization troubles were not more serious than in American practice. It is specifically stated that there was no trouble due to polarization or falling off of efficiency.[84] The only trouble reported is cracking of the carbon, which is attributed to penetration of electrolyte and expansion of corrosion products, but might, perhaps, be due to the swelling and disintegration which has been reported to occur with graphite at lower hydrogen fluoride concentrations. In referring to the procedure when new anodes are installed, it is remarked that hard anodes are attacked mainly by erosion, that erosion leads to accumulation of carbon particles, while corrosion leads to accumulation of magnesium fluoride and fluosilicate, and this mixed sludge is cleaned out when new anodes are being installed.

Of the high temperature cells, the German, called the Falkenhagen cell,

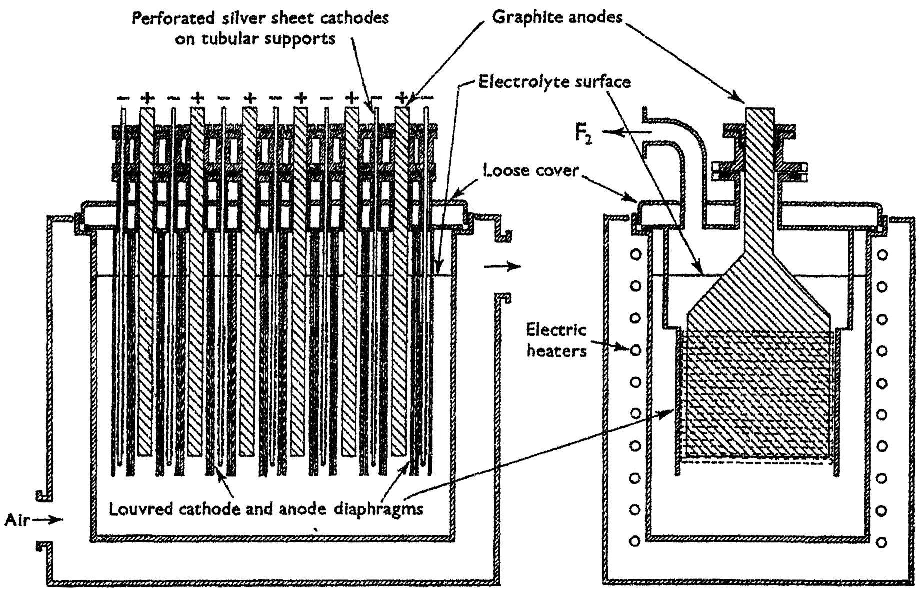

Fig. 14. FLUORINE CELL: FALKENHAGEN OR O.K.H.

from the place of its installation, is notable for its extensive use of magnesium alloy, as in the I. G. cell. It represents the largest and most ambitious fluorine cell installation which has been described.[84, 85] A complete plant with 60 cells, for the production of 720 tons of fluorine per annum, to be converted into 1000 tons of chlorine trifluoride, was erected during the war. A great deal of research had gone into the design of the cell, some account of which has been given by an allied investigator,[85] but little by those who had actually participated in the work. With its silver cathode, it seems to be a descendant of the Bodenstein cell[55] although it had not the other outstanding feature of that earlier cell, bottom entry electrodes. The Falkenhagen cell (Fig. 14), of 2500 amp. maximum capacity, had a container 45 in. × 27 in. × 38 in. deep, welded from ¼ in. magnesium alloy sheet, standing in an outer casing, with provision for electric heating when the temperature fell below 245°, and air cooling when the temperature rose above 253°. The six graphite anodes and seven perforated corrugated silver sheet cathodes were surrounded by cast magnesium alloy bells, louvred in the facing sections. The anode passed through a neck in the bell, closed by a gland and insulated by a cement of fluorspar, red lead and glycerine. The maximum anodic current density was 73 amp. per sq.ft., the current efficiency 95%. Each cell had its own D.C. rectifier, normally worked at 2000 amp., and at the start of its life would require 6·0 – 6·5 volts. The cell voltage slowly increased owing to anodic polarization, and when it reached 11·5 volts, after 3 – 4 months of continuous operation, a special generator was connected to apply 60 volts, at which the cell took 5000 amps.

After 5 – 10 minutes of this treatment the anode would operate again at low voltage. Sometimes, however, it is said, the anode had to be removed and scraped to restore its normal properties.

Very special care was taken in the preparation of electrolyte and the treatment of hydrogen fluoride for the cell feed. The pure potassium bifluoride was pre-electrolyzed in a magnesium cell, with graphite anodes and copper cathodes, to remove the last traces of water as well as undesired impurities, and run into magnesium containers for storage. Owing to corrosion of the silver cathode and accumulation of sludge, the electrolyte was removed from the cell at 12 – 18 months intervals and clarified by settling before returning to the cell. The anhydrous hydrogen fluoride contained up to 0·8% of silicon tetrafluoride, up to 0·5% of sulphur dioxide and small amounts of water. It was treated with 1 – 2% of fluorine at 250 – 300°C. to decompose sulphur dioxide and traces of water, and recondensed. The cells were supplied continuously with hydrogen fluoride gas through a magnesium distributor in the cathode compartments; each cell stood on a weighing machine so that the rate of addition could be controlled, but a check analysis of the electrolyte was made every three days, and the hydrogen fluoride content of the hydrogen, recorded catharometrically, was also a guide to electrolyte composition. The hydrogen and the fluorine were cooled to -60°C. to remove hydrogen fluoride, and the fluorine then contained about 1% of impurities, mainly oxygen, carbon tetrafluoride and silicon tetrafluoride.

The American installation of high temperature cells had seven cells each of 800 amp. maximum capacity,[95] and a notable feature was the high anodic current density. The cell had a narrow container of Monel metal 4 in. × 34 in. × 16 in. deep, with a jacket filled with heat transfer fluid (diphenyl oxide). The container was the cathode, and there were 16 graphite rods, 1 in. in diameter, fitted in the copper head of the anode assembly. Although a diaphragm was not necessary to separate the gases generated at anode and cathode, a cage of Monel metal strip was attached to the gas separating bell, to prevent broken anodes causing electrical short circuits, and this carried a deflector plate to stop hydrogen from the cell bottom rising into the fluorine compartment. The cell operated at 260 – 270°C., the anodic current density was 300 – 325 amp. per sq.ft., and the normal voltage 6 to 8 volts. The current efficiency, normally 90 – 95%, dropped as the anode aged to 55%, but this could not be explained. Hydrogen fluoride was passed into the cell bath at regular intervals. There was some corrosion of the metal parts, not regarded as serious, but a sludge of metal fluorides accumulated in the bottom of the cell and was removed when an anode assembly was changed. The limiting factor in the life of a cell was deterioration of the anode contact. Some anodic polarization occurred, and was cured by raising the voltage to about 30, when the current suddenly increased and normal operation at about 8 volts could be resumed.

The industrial development of fluorine has continued since the end of the war, and manufacturing developments in U.S.A.[96] and in Great Britain[97] have been described. The Pennsylvania Salt Manufacturing Co., whose 250 amp. cell has been referred to above, have developed a 2000 amp. cell of similar design. A specification is given for electrolytes, the impurities in which may not exceed the following proportions:- potassium fluosilicate 0·2%, sulphate 0·1%, chloride 0·05%, and water 0·05%. The hydrogen fluoride used should not contain more than 0·2% of water, 0·1% of hydrofluosilicic acid, 0·06% of sulphur dioxide, and 0·005% of sulphuric acid. A laboratory cell using a bottom entry anode in medium temperature electrolyte at 40 amp. has been described[98] and a French laboratory installation may also be noted.[99]

Some further information has been given regarding the laboratory cell supplied by the Harshaw Company[100] and it has been said that cells have also been supplied by an English company.[101]

THE CHEMICAL BEHAVIOUR OF CARBON ANODES IN FLUORINE CELLS.

It has been remarked that the anodic behaviour of carbon and graphite in the fluorine cell electrolyte is complex, and some understanding of these phenomena can be obtained from the chemical and physical relations of carbon and fluorine, though the explanation is as yet far from complete. Ruff and Bretschneider[102] in 1934 showed that at temperatures of 400° and above, carbon in its various forms reacts with fluorine to give a solid product corresponding in composition to carbon monofluoride, CF. Later W. and G. Rüdorff[103] showed that hydrogen fluoride catalyzed the reaction, so that graphite (natural flake) in presence of fluorine and sufficient hydrogen fluoride forms carbon monofluoride at temperatures as low as 250°C. This product is an electrical non-conductor, and it was suggested that its gradual formation may explain the slow polarization which has frequently been reported in high temperature cells. The same workers showed that fluorine in the presence of hydrogen fluoride vapour reacts with graphite at temperatures below 100°C., to form a solid, approximating to tetracarbon monofluoride, C_4F, with a somewhat different structure from carbon monofluoride.[104] This compound is formed readily at room temperature but not at all above 100°C., and in this temperature range the compound itself decomposes. Moreover, in liquid hydrogen fluoride, fluorine converts graphite into an unstable salt-like compound for which the formula $(C_{24}^{+})HF_2^{-},4HF$ and the quite inappropriate name of 'graphite bifluoride' have been proposed.[105] The tendency of graphite, when anodic, to swell and disintegrate in electrolytes richer in hydrogen fluoride, and of even amorphous carbon to polarize in medium temperature electrolyte, must be related to the formation of these compounds. The significance of carbon monofluoride formation in the high temperature cell has been considered in a further paper by Rüdorff and others.[106] The gradual increase in voltage in such a cell, called the 'ageing phenomenon', is attributed to the superficial formation of carbon monofluoride having insulating properties. At a certain point the voltage rises discontinuously and the anode effect sets in, while luminous phenomena occur around the anode owing to actual combustion of the carbon monofluoride to volatile fluorocarbons, mostly carbon tetrafluoride. This explains the procedure used to cure polarization in the Falkenhagen cell. This burning produces a highly polished, mirror-like appearance on the anode surface, which was, earlier, attributed to a deposition of silicon.

The physical behaviour of the fluorine discharged at a carbon anode in a medium temperature cell has been described by Rudge and co-workers.[107,108] Medium temperature electrolyte has a contact angle greater than 90° at a carbon anode, and as a consequence of this, fluorine discharged at the surface does not form spherical bubbles breaking away from the surface, but accumulates as lenticular pockets pressed against the surface. These slip up the anode surface, and fluorine escapes at the anode-electrolyte meniscus, which is negative. This is a development of the non-wetting observations of Fredenhagen and Krefft, and of Cady *et al.*, and explains why a diaphragm can be dispensed with in the medium temperature cell. These observations have led to a novel proposal for taking fluorine from the cell (see Patents).

PATENTS.

Several of the features in the wartime and post-war development of fluorine production considered above have been the subject of patent applications. The use of lithium fluoride in amounts of about 4% is claimed to render the use of a carbon anode possible in a medium temperature cell.[109]

The dehydration of electrolyte by distilling off part of the hydrogen fluoride has been claimed.[110] The use of a carbon anode impregnated with 35 – 47% of copper, in an electrolyte containing 0·1 to 2·5% of lithium fluoride, at temperatures between 95° and 115°C. has been protected,[111] and a carbon anode (which may be copper impregnated) provided with a thin coating of metallic nickel is claimed to improve operation initially, when there is residual water in the electrolyte.[112] In two patents, claims are made for the use of a subsidiary nickel anode when the carbon anode becomes polarized.[113] Particular cell designs have been patented[114] including one medium temperature cell with nickel anodes[115] and one with a method of operation specified.[116] A patent of English origin claims that polarization troubles in the medium temperature cell are overcome by the use of a carbon of much greater permeability than ordinary carbon.[117] A combination of this high permeability carbon and the non-wetting effect reported by the same workers, leads to a novel arrangement of cell in which the anode, which is hollow and provided with access to the interior by means of a copper pipe, is wholly immersed in the electrolyte.[118] The copper provides electrical connexion to the carbon, but itself, as is already known, is passive. The fluorine appears in the interior of the anode and is led away by the copper pipe (Fig. 15).

A patent for the production of uranium by electrolysis of uranium tetrafluoride in a bath of mixed halides, e.g. calcium and sodium chlorides,

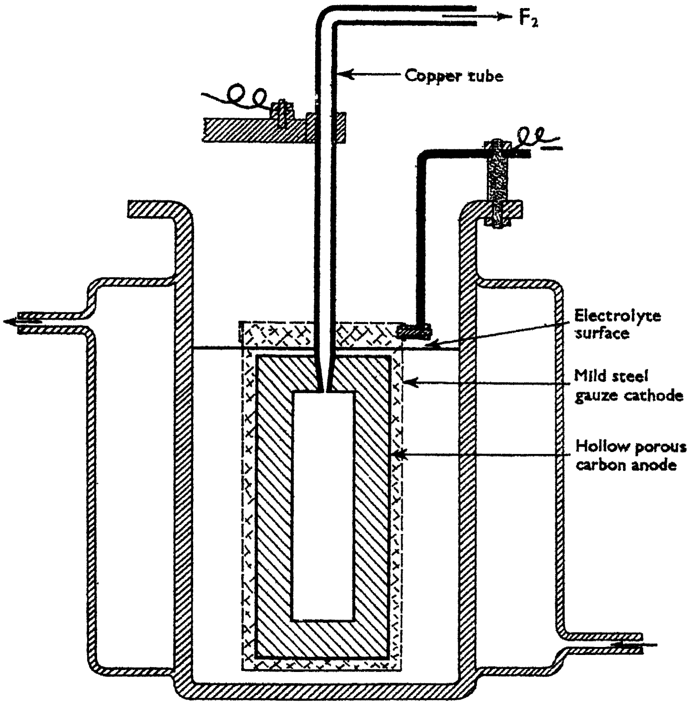

Fig. 15. FLUORINE CELL WITH HOLLOW CARBON ANODE

claims that fluorine is released, contaminated with a small amount of chlorine,[119] but the reliability of this observation is perhaps doubtful.

BOTTLED FLUORINE

It has been noted above how the study of fluorine has been progressively facilitated by the increasing availability of compounds required in its preparation. Moissan's raw material was aqueous hydrofluoric acid, from which he had to prepare potassium bifluoride and thence anhydrous hydrogen fluoride and fluorine. In the 1920's it was possible to buy potassium bifluoride, in the 1930's, anhydrous hydrofluoric acid, and finally, in that decade also fluorine itself became available. There have been references to compressed fluorine in steel cylinders, supplied by I. G. Farbenindustrie before the war of 1939–45.[120] During the war supplies of this kind were developed in America for the special requirements of the Manhattan Project,[82,83] and since the war supplies have become commercially available in U.S.A.[96] and in Great Britain.[97,121]

The mechanical compression of fluorine has been studied. Problems of lubricant and gland packing in the more conventional type of equipment were very serious, but compressors of the diaphragm type have been used successfully up to 40 lb. per sq. in.[122-3] At this pressure the amount which can be contained and transported in steel bottles is very small, so higher pressures are essential and to achieve them the procedure adopted is to liquefy the fluorine by cooling with liquid nitrogen and then to re-evaporate the gas to the desired pressure in the shipment container. Several descriptions have been given of the equipment used in this process.[84-6,124-5] Before the fluorine is liquefied it is desirable to reduce the hydrogen fluoride content to a very low figure. For this purification, sodium fluoride has generally been used to absorb the hydrogen fluoride, although potassium fluoride has sometimes been employed. Occasionally workers have cooled the fluorine to -80°C. by means of solid carbon dioxide-acetone mixtures, but the amount of hydrogen fluoride remaining in the gas at this temperature is still appreciable,[125] sufficient, as Moissan showed, to cause a slight attack on glass.[126] For still more efficient purification by cooling, liquid air has been used. Ruff showed, however, that the condensate collecting in the liquid air traps tends, on warming up, to explode; the unstable compounds causing this were not identified, but were destroyed by prior heating to 300°C.[94] In a process involving liquefaction and re-evaporation of the fluorine, as in the preparation of bottled fluorine, there would be a tendency for such explosive residues to accumulate, and it is therefore standard practice to heat the gas to 300°C. before liquefaction. The purification of fluorine from the oxygen it usually contains has been described.[59] The gas is treated by selective absorption of oxygen on active charcoal at low temperatures and is then condensed and fractionally distilled at liquid air temperature, the fluorine content by this means being increased from 95% to 99%. (See also difluorine dioxide, page 193). It is possible to reduce the hydrogen fluoride content to a fraction of 1% by passage over sodium fluoride, and the performance when the sodium fluoride is used regeneratively has been studied.[125] It has been proposed also to make a porous absorbent by compressing sodium acid fluoride, NaF.HF, into pellets, which are then filled into a tower and heated at 275–300°C. in a stream of nitrogen to remove the hydrogen fluoride and leave a porous pellet. The tower is operated for hydrogen fluoride absorption at 100°C., to prevent blockages occurring owing to swelling of the pellets or formation of liquid higher hydrofluorides. Such a tower should serve for many cycles of absorption at 100°and regeneration at 275–300°C., without any falling off in performance.[125]

Bottled fluorine is potentially a very dangerous material to handle. If for any reason a small amount of reactive material causes a local reaction with fluorine to occur, this will most probably be in the valve, expecially in the gland. The heat evolved in any such reaction is considerable, and may cause a rise in temperature sufficient to start an uncontrollable reaction between the fluorine and the gland packing, and even the metal of the valve itself may finally burn briskly in the high concentration of fluorine which is available. Illustrations of this effect have been given.[125] Because of this risk, American practice limited the pressure in the containers to a maximum of 400 lb. per sq. in., and recommended that the containers should be used behind stout brick or steel barriers, with remote control of the valves.[96] In Germany, cylinders were filled to 2000 lb. per sq. in., and no information has been given on any safety precautions recommended. An American patent describes a tank for storing fluorine, made of copper or nickel or a binary alloy, but the particular advantage over mild steel is not obvious.[127]

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SECTION II

THE PHYSICAL AND CHEMICAL PROPERTIES OF FLUORINE

By H. R. LEECH

[In part with K.D. WADSWORTH]

THE PHYSICAL PROPERTIES OF FLUORINE

The melting point of fluorine has been given as -223°C.[1] but a more recent and probably a more accurate determination gives 55·2°K. (or -217·9°C.)[4] The heat capacity of the solid has been estimated to be 27·5 joules per gram atom,[3] i.e. 13·14 g.-cal. per mol., but lower figures are given by the series of determinations carried out by Kanda[2] given in Table I. The latent heat of fusion has been determined calorimetrically as 372 g.-cal. per mol.[2] or, calculated from the vapour pressure data, 390 g.-cal.,[4] and the heat of vaporisation of the solid, 1970 g.-cal. per mol.[4] The vapour pressure of the solid is given as:-[4]

Temperature, °K	51·85	52·55	53·90	54·50	55·15
Vapour pressure, mm. of mercury	0·10	1·55	1·75	2·10	2·70

These data are represented by the equation $\log_{10} p_{mm} = -\frac{430{\cdot}06}{T} + 8{\cdot}233$. The characteristic temperature θ of the solid is 100·3.[2]

From determinations of the vapour pressure of liquid fluorine, the following equations have been derived, p_{cm} being the vapour pressure in cm. of mercury and T the temperature in °K.

$$^{5}\log_{10} p_{cm} = 7{\cdot}3317 - \frac{406{\cdot}8}{T} - 0{\cdot}007785\,T$$

$$^{6}\log_{10} p_{cm} = 8{\cdot}7202 - \frac{462{\cdot}66}{T} - 0{\cdot}01656\,T$$

$$^{4}\log_{10} p_{cm} = 8{\cdot}1975 - \frac{442{\cdot}72}{T} - 0{\cdot}013150\,T$$

From these equations the corresponding atmospheric boiling points are, respectively, 84·93°, 85·21°, 85·19°K., or about -188°C. The critical temperature was found to be 144°K., or -129°C., and the critical pressure estimated to be 55 atm.[5] The latent heat of vaporization at the normal boiling point, calculated from the above vapour pressure data, is given as 1600,[5] 1560[6] and 1581[4] g.-cal./mol.

TABLE I.– MOLAR HEAT CAPACITIES OF SOLID AND LIQUID FLUORINE[2]

Temperature, °K.	14·91	17·75	20·01	23·10	25·42	29·50	32·00	35·40	39·11	43·10
Ht. capacity, g.-cal./mol.	1·167	1·807	2·240	2·841	3·440	4·310	4·795	5·561	6·280	7·120
°K.	47·95	52·98	53·98	55·20	57·50	62·51	67·49	77·10	83·41	85·19
g.-cal./mol.	7·741	8·210	8·761	m.p.	10·84	10·92	10·98	11·12	11·20	b.p.

The extensive determinations by Kanda have also given the data in Table II for the density, dielectric constant and surface tension.

PROPERTIES OF LIQUID FLUORINE

TABLE IIa

Temp. °K.	Density[7] g./cc.	Dielectric Constant[7] K
57·40	1·204	1·567
60·51	1·195	1·561
64·41	1·185	1·553
68·38	1·154	1·546
73·00	1·141	1·536
75·01	1·136	1·533
79·40	1·124	1·524
83·21	1·113	1·517

TABLE IIb

Temp. °K.	Surface Tension[8] dynes/cm.
57·10	14·61
59·95	14·16
61·41	13·85
64·20	13·46
65·30	13·17
71·00	12·20
72·11	12·10
76·30	11·40
81·50	10·41
84·91	9·85

The solubility of chlorine in liquid fluorine has been reported,[9] and the viscosity of gaseous fluorine determined by the same worker[8] is given in Table III.

TABLE III. – VISCOSITY OF GASEOUS FLUORINE[8]

Temperature, °K.	86·8	118·9	148·8	167·9	192·3	213·1	229·6	248·9	273·2
Viscosity, poises × 10^{-5}	5·55	8·75	10·80	12·01	13·79	14·92	16·11	17·27	20·93

From these data a value of 3·65 A. for the effective diameter of the fluorine molecule was calculated. Compilations of thermodynamic functions for gaseous fluorine have been given,[10,11] and some data from these[11] are given in Table IV.

TABLE IV. – THERMODYNAMIC FUNCTIONS FOR GASEOUS FLUORINE, cal./mol.

T, °K.	$-\frac{F_0-H_0^{\circ}}{T}$	S°	C_p°
298·16	41·412	48·484	7·466
300	41·455	48·530	7·474
400	43·510	50·734	7·853
500	45·139	52·519	8·135
600	46·498	54·020	8·331
800	48·696	56·453	8·566
1000	50·446	58·379	8·691
1200	51·905	59·970	8·763
1400	53·156	61·325	8·809
1600	54·253	62·503	8·839
1800	55·228	63·546	8·860
2000	56·108	64·480	8·876

The thermal conductivity of fluorine has been determined[12] between 93° and 787°K., in connection with the determination of the heat of dissociation, using fluorine made by the decomposition of chlorine trifluoride as described previously (see page 17). The results are given in Table V. From these results a value of 3·52 A. for the effective diameter of the fluorine molecule is calculated. It was also concluded that the heat of dissociation cannot be less than 45 kg.-cal./mol., but this is higher than the most probable value, and the work has been criticised by Evans *et al.* (see below, page 49) who suggest that any attack of fluorine on the heated nickel filament, which cannot be excluded, would falsify the results. The presence of traces of chlorine in the fluorine (from the method of preparation employed) would probably catalyze such an attack.

TABLE V – COEFFICIENTS OF THERMAL CONDUCTIVITY FOR FLUORINE GAS, IN 10^{-7} cal./cm. degree sec.

T°K	100	150	200	250	273	300	350	400	450	500	550	600	650	700	750	800
λ	206	321	436	544	592	643	736	823	909	993	1078	1166	1251	1336	1418	1503

It has been suggested that ortho- and para- systems may be expected not only in the hydrogen molecule, but in a number of others including fluorine, for which the ratio of ortho to para is probably 3.[13] Several workers have discussed the electronic structure of the fluorine molecule and compared it with the nitrogen and oxygen molecules.[14]

The heat of dissociation of fluorine has been a subject of some interest in the last decade. The estimate of von Wartenberg and Taylor, giving 63·5 kg.-cal./mole, was based on an extrapolation from the spectral data for the other halogens, and was a very empirical value.[15] Nevertheless, it fitted in very reasonably with the known dissociation energies of the other halogens: 57·2, 46·1, and 35·5 for chlorine, bromine and iodine respectively,[16] and not too badly with earlier estimates, and this figure was generally accepted. A number of other estimates were made, which generally, up to 1940, did not differ widely from von Wartenberg's figure. Table VI shows all the values.

TABLE VI – THE DISSOCIATION ENERGY OF FLUORINE $D_0(F_2)$

Year	Authors	Ref.	Value Kg.cal./mol.	Method
1922	Henglein	17	64	Extrapolation from dissociation of other halogens, and atomic radius.
1925	Wilsdon	18	316.5	Estimated from electronic theory.
1927	Gale and Monk	19	>69	From spectra; no actual figure given.
1930	Stäckel	20	69	Estimated from electronic theory.
1930	v. Wartenberg & Taylor	15	63.5	Extrapolation from spectra of other halogens.
1932	Desai	21	76	Born-Haber cycle with NaF, KF.
1932	Lederle	22	67	Extrapolation, spectral data of other halogens.
1937	Bodenstein & Jokusch	23	70	Further examination of Wartenberg's method.
1939	Herzberg	24	64	Spectral.
1940	Clark	25	81	Spectral and theoretical considerations.
1942	Wahrhaftig	26	? 8.6	Spectrum and thermochemistry of ClF.
1947	Schmitz & Schumacher	27	30-33	Spectrum and thermochemistry of ClF.
1951	Schumacher	28	30	Estimated from thermochemistry of F_2O.
1948	Wicke	29	63	Thermal conductivity of fluorine.
1950	Eucken & Wicke	30	40.2	Review of data.
1951	Wicke & Franck	31	>45	Thermal conductivity.
1948	Gaydon	32	50	Review of data.
1949	Glockler	33	60	Heat of dissociation of ClF.
1950	Caunt and Barrow	34	50	Modified Born-Haber cycle with RbF, CsF.
1950	Caunt and Barrow	35	<45	Modified Born-Haber cycle with TlF.
1950	Butkov & Rozenbaum	36	72	Estimate from data on spectra and force constants.
1950	Evans, Warhurst and Whittle	37	37	Re-evaluation of thermochemical and spectral data.
1950	Nathans	38	30-40	Consideration of Wicke's data.
1951	Johnston	39	18	Estimation of electron affinity.
1951	Doescher	40	37.7	Measurement of dissociation pressure.

From a study of the absorption spectrum of chlorine monofluoride, and its heat of formation, Wahrhaftig concluded that $D_0(F_2)$ must be smaller than was generally believed: the determined value for the heat of formation of chlorine monofluoride led to the very low value of 8·6 kg.-cal./mole for $D_0(F_2)$, and he concluded that the heat of formation of chlorine monofluoride also required revision. A lower value for Q_F (ClF) was shortly afterwards determined,[27] giving a value for $D_0(F_2)$ between 30·6 and 33·4. Wicke, applying the data for the thermal conductivity of fluorine, at first said that this result supported the value of 63 kg.-cal., but this figure was later revised towards much lower values. A critical review by Evans, Warhurst and Whittle showed that the best estimate gave 37 ± 8 kg.-cal., and shortly afterwards the figure 37·7 kg.-cal., based on the actual determination of the dissociation pressure, was published. It seems probable, therefore, that the heat of dissociation of fluorine $D_0(F_2)$, cannot be very far from 37 kg.-cal./mole. The determination of the dissociation pressure was carried out in a nickel vessel coated stepwise with fluoride by heating in contact with fluorine at temperatures up to 850°C., using a differential manometer filled with a fluorocarbon oil. The variation of pressure with temperature over the range 486°–842°C. was compared for fluorine and for nitrogen, and a straight line relation established for

$$\frac{\ln p_F^2}{\ln p_{F_2}} = \ln Kp = 14.5 - \frac{19{,}000}{T} \quad (p.\ \text{in atm.})$$

Using this isochore, the calculated temperatures for various degrees of dissociation at various total pressures are as given in Table VII, linear interpolation for intermediate degrees of dissociation being of about the same accuracy as the experimental data. Temperatures outside the range of Doescher's measurements (486–842°C.) are bracketed.

TABLE VII – DISSOCIATION OF F_2 – TEMPERATURES (°C.) FOR GIVEN DEGREES OF DISSOCIATION AT GIVEN TOTAL PRESSURE.

Degree of Dissociation, %	Pressure, mm. Hg.			
	760	100	10	1
0·1	(430)	(380)	(330)	(290)
1	580	510	(440)	(380)
10	800	690	590	510
50	(1060)	(900)	750	640
90	(1350)	(1120)	(910)	760
99	(1780)	(1420)	(1130)	(920)

The implications of this much lower value for the heat of dissociation of fluorine have been reviewed by Evans *et al.*[37]

INTER-ATOMIC DISTANCE.

The inter-atomic distance in the fluorine molecule has been determined by electron diffraction, and a figure of 1·435 ± 0·010 A. obtained[41] as against an earlier, provisional figure of 1·45 ± 0·05 A.[42] This gives 0.72 A. for the covalent radius of fluorine, and Pauling[43] has pointed out that there is an unexplained discrepancy between this figure and the 0·64 A. for the normal single bond covalent radius for fluorine deduced from crystallographic data. Doubt has been cast on the value 0·64 A.,[44] and Gordy, having revalued the data, more particularly for fluorine covalent double bonds, proposed the figure 0·60 A.[45] Some success has been achieved in relating the data for bond distance to atomic structure, by general formulae applicable not only to fluorine;[46] in one case the formula gives a value of 1·42 A. for the F–F distance.[47] The interpretation of the parachor as a measure of atomic volume has been applied to fluorine, introducing the 'packing radius' in addition to the 'bond radius'. Taking the Pauling value of 0·64 A. for the latter, parachor data give 1·16 A. for the packing radius of fluorine, which agrees well with the value of ½ (F – F) in carbon tetrafluoride, which is 1·12 A.[48] More general discussions have also attempted to deal with the bond radius of fluorine.[49]

ELECTRON AFFINITY

This, like the dissociation energy, has been a controversial subject. A value of about 95 was at one time generally accepted, because it fitted in as would be expected with the other halogens. The following two series have been quoted (kg.-cal./g.-atom).

	fluorine	chlorine	bromine	iodine
Sherman[50]	98·5	92·5	87·1	79·2
Mayer and Helmholtz[51]	95·3	86·5	81·5	74·2

The electron affinity may be related to the dissociation energy in a Born-Haber cycle.[37]

$$E_x = Q(\mathrm{MX})_c + S(\mathrm{M})_c + I(\mathrm{M}) + \tfrac{1}{2}D(\mathrm{X}_2) + U_0$$

where E_x is the electron affinity of the halogen X, $Q(\mathrm{MX})_c$ the heat of formation of the crystalline salt MX from crystalline metal and gaseous halogen molecules, $S(\mathrm{M})_c$ the heat of sublimation of the alkali metal, $I(\mathrm{M})$ the ionization potential of the alkali metal, $D(\mathrm{X}_2)$ the halogen dissociation energy, and U_0 the lattice energy of crystalline MX. This method was used to obtain the results for the halogens quoted above, and the generally accepted value of 95·3 kg.-cal. for fluorine is based on the von Wartenberg value for $D_0(\mathrm{F}_2)$ of 63·5. Correcting to the new value of 37·7 kg.-cal., the electron affinity becomes 82·4 kg.-cal.[52] An attempt had been made to determine the electron affinity experimentally, from the performance of a tungsten filament in fluorine at temperatures up to 2600°K., but the results were considered anomalous because of the wide scatter of the data and the apparent trend with temperature.[53] A re-examination of the results shows that the mean value of 27 observations is 82·2 kg.-cal., in good agreement with the value arrived at above.[52] This, then, must be accepted as the electron affinity of the fluorine atom. Evans *et al.*[37] have also arrived at this figure in a re-assessment of the data for the alkali metal fluorides, and show that the results are remarkably consistent, being

from	LiF	NaF	KF	RbF	CsF
E_0, kg.-cal.	81.8	82.0	79.3	83.1	82.5

A more recent attempt to estimate a value by quantum mechanical methods and extrapolation from spectroscopic data gives a figure of 73 kg.-cal.[39] Earlier applications of a Born-Haber cycle had given values of 94 kg.-cal.[54] and 92.2 kg.-cal.[55] An alternative method of approach, by extrapolation from ionization potentials, has given values of 80.7,[56] 91,[57] 94.5,[58] and 94.5.[59] Other methods gave false results.[60]

OTHER CONSTANTS

Pauling's electronegativity function for fluorine was found to be 4.0,[43] which was confirmed by a rather different method of derivation.[61] More recently a revised value of 3·9 has been proposed.[62] From a study of the reactions of metal fluorides and hydrogen, values for the chemical constants of fluorine and hydrogen fluoride are respectively 0·7 ± 0·3 and −1·0 ± 0·3.[63]

The value of the normal electrode potential of fluorine has been estimated from thermochemical data to be 2·85 ± 0·04 v.[64] An attempt to determine this experimentally by measurements on the cell F_2,Pt/KF in HF/PbF_2,Pb was unsuccessful. No constant readings were obtained, apparently owing to attack on the platinum electrode by the fluorine.[65] Further determinations of the *E.M.F.* of hydrogen–fluorine cells are reported later. Measurements in fused fluorides have led to a value for the fluorine potential at 18°C., referred to hydrogen as zero, as 1·923 v.[66] but there has been controversy on this point.[67]

NUCLEAR MAGNETIC MOMENT

Studies[68] of the hyperfine structure of the arc and band spectra of fluorine indicated that the nuclear spin quantum number was ½ and the nuclear magnetic moment about 3 nuclear magnetons. Millman *et al.*[69,70] have made quantitative determinations by the molecular beam resonance method, the most recent[70] being + 2·625 ± 0·003 nuclear magnetons. Determinations by the same method by Siegbahn and Lindström[71] and by Poss[72] gave 2·626 while a determination of the ratio of the precession frequencies for hydrogen and fluorine[73] yielded the slightly higher value 2·627 nuclear magnetons.

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ATOMIC WEIGHT

The determinations of Moles and Batuecas[1, 2, 3] in 1920 – 1922 of the gas density of methyl fluoride which gave F = 19·002 ± 0·004, were repeated by Patterson, Cawood and Whytlaw-Gray[4,5,6] in 1931 – 1932 who found F = 19·001 using different samples of methyl fluoride prepared by heating tetramethylammonium fluoride, and by the reaction of potassium methyl sulphate with potassium fluoride. This result, which suggested the existence of a higher isotope of fluorine, contrary to the findings in 1920 of Aston,[7] was disputed by Batuecas[8] and by Moles[9,10] who contended that the methyl fluoride used by Patterson *et al.* was impure. Further gas density determinations by Cawood and Patterson[11,12] in 1935 – 1936 on methyl fluoride and carbon tetrafluoride gave F = 18·997 and 18·995 respectively.

Mass spectrographic determinations by Aston[13] gave 19·0045 for F on the physical (O^{16} = 16·0000) basis, equivalent to 18·9994 on the chemical basis. In 1937 – 1938, Moles[14,15] and Moles and Toral[16] determined the gas density of silicon tetrafluoride and deduced F = 18·995 ± 0·001, assuming the recently found value for silicon of 28·104 instead of the then accepted international value of 28·065. Keesom,[17] using a different method of extrapolation to zero pressure for Moles's results on the gas density of silicon tetrafluoride, obtained F = 18·998.

More recently (1941 – 1945), determinations of the atomic weight have been made by Hutchinson and Johnston[18-22] by the pykno-*X*-ray method in which the densities and lattice constants of lithium fluoride were compared with those of calcite, diamond, sodium chloride and potassium chloride. The weighted average value of these determinations[22] is F = 18·9967 ± 0·0010. This is significantly lower than the value of 18·9994 found by the mass spectrographic method by Aston (see above) and also more recently derived by Tollestrup, Fowler and Lauritsen[23] from the energy release in several nuclear reactions involving fluorine.

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THE CHEMICAL PROPERTIES OF FLUORINE

The preceding sections indicate the relatively restricted state of knowledge of the chemistry of fluorine at the time when Mellor's Comprehensive Treatise was written. This deficiency is most startling in dealing with the chemical properties, and attention must be drawn to the many contradictions of statements made in the main work, which are required as a result of the developments of the last thirty years. Well did Mellor quote Moissan's *l'étude des composés fluorés réserve encore bien des surprises.* Thus fluorine does not inevitably react with hydrogen, a definite initiation is required; oxygen compounds of fluorine *have* been prepared; chlorine and fluorine *do* react when heated together, as do nitric oxide or nitrogen peroxide and fluorine. Silica does *not* react energetically with fluorine in the cold. Pure carbon does *not* react with fluorine at the temperatures stated, 50 – 100°C., and the whole of the section on the reactions of fluorine with carbon and carbon compounds requires revision. Lastly it should be remarked that metals are in general *not* attacked by fluorine at ordinary temperatures.

It has been pointed out by von Wartenberg[1] that there has been a tendency to overestimate the reactivity of fluorine, and to underestimate its affinity. 'Fluorine develops by far the largest heat of reaction, but, contrary to a widespread idea, generally reacts rather slowly. When, however, reaction does occur it is violent owing to the high heat evolution, so that the well-known illusion of a high reactivity arises'. It may be of interest here to note some heats of reaction (all in kg.-cal.):-

$$\begin{array}{llll}
H_2 + F_2 \rightarrow 2HF_G + 128{\cdot}4 & & H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O_G + 57{\cdot}8 \\
C + 2F_2 \rightarrow CF_4 + 231 & & C + O_2 \rightarrow CO_2 + 94{\cdot}0 \\
Na + \tfrac{1}{2}F_2 \rightarrow NaF + 136{\cdot}0 & & Na + \tfrac{1}{2}Cl_2 \rightarrow NaCl + 98{\cdot}3 \\
Si + 2F_2 \rightarrow SiF_4 + 370 & & Si + 2Cl_2 \rightarrow SiCl_{4G} + 145{\cdot}7
\end{array}$$

$$Si + O_2 \rightarrow SiO_{2X} + 205$$

(The heats of formation of fluorine compounds have been reviewed by Wicke.[2])

Fluorine does, however, react very readily with moisture and with moist materials, and with organic matter generally, such as oil and grease, rubber and textiles. In working with fluorine, therefore, it is necessary to select materials outside this group, but it has been seen already that there remains a wide range of materials which can be used in contact with fluorine with safety, including most metals, ceramics, and siliceous bodies (see page 17). The development in recent years of fluorocarbons, of fluorochlorocarbons, and of polymers of such compounds as tetrafluoroethylene and chlorotrifluoroethylene, all reasonably resistant to fluorine, is increasing the range of materials available. Reference has already been made to patents covering the preparation of special materials for use in fluorine cells, and others have been taken out for conditioning packing materials to make them resistant, by controlled treatment with fluorine,[3] and for making filling materials from mixtures of inorganic fluorides and higher fluorocarbons.[4] One problem arising in work on fluorine is the safe disposal of an excess of it, and this has been done by passing the fluorine into a gas burner, fed with coal gas or, e.g., propane, and washing out with water and dilute caustic soda the hydrofluoric acid thus formed.[5]

Reference has already been made to the liquefaction of fluorine and to the care needed in permitting materials to come into contact with the liquid. Cotton gave a violent explosion, whilst neoprene rubber gave but a slight explosion and leather only smouldered and charred.[6] It has been considered whether liquid fluorine could be used as one constituent of a fuel in rocket propulsion.[7] The reaction of solid fluorine with liquid hydrogen has been studied[8] and it was found impossible to reproduce the immediate violent explosion reported earlier by Dewar and Moissan. Explosions did sometimes occur, but on other occasions even when the mixture was exposed to direct sunlight, there was no explosion. These experiments did not appear to support the suggestion which had been made (see below) that the explosions can be attributed to the presence of contaminant, especially organic matter. It was also reported that mixtures of carefully dried hydrogen and fluorine were non-reactive, even when exposed to ultra-violet light.[9] Eyring and Kassel confirmed this,[10] and found that mixtures could be kept for half an hour at ordinary temperatures without explosion occurring. They considered that the thermal reaction by way of atoms should begin at 150 – 250° (although this view would require revision in the light of the lower value now accepted for the heat of dissociation of fluorine). But the thermal reaction certainly cannot occur at liquid hydrogen temperatures, unless initiated by a very active catalyst, static electrical discharge, or other extraneous cause. Later work has shown in detail how the tendency to explosion in hydrogen–fluorine mixtures depends on the state of the walls of the containing vessel.[11] The reaction, it has been concluded, is a chain reaction involving atoms, as in the case of the other halogens, and the chains are very easily broken at the wall.[12]

A welding torch using a hydrogen–fluorine flame has been described and its use for welding copper patented.[13] (A chlorine trifluoride–hydrogen torch and its similar use has also been described).[14] The temperature of the hydrogen–fluorine flame, with equal proportions of the constituents, has been estimated to be 4300°K., and the temperature as measured by the line reversal technique using solar radiation as source agrees with this.[15] It is interesting to note here that in a hydrocarbon–fluorine flame, ignition was spontaneous with unsaturated and aromatic hydrocarbons, but not always so with paraffinic hydrocarbons. A slight contamination of the burner tip was, however, sufficient to cause apparently spontaneous ignition.[16] In this investigation it was again found that hydrogen does not ignite spontaneously with fluorine.

The action of fluorine on water and aqueous solutions has been the subject of extensive researches by Fichter,[17-40] and has been studied by a number of other workers.[41-46] Thus Fichter stated that when fluorine is added steadily to water at 0°, hydrogen peroxide is first formed, but after 20 minutes the concentration of peroxide diminishes and oxygen and ozone are evolved.[17] Cady found that there was very little if any ozone, but that the reaction products besides hydrogen fluoride were hydrogen peroxide, oxygen, and the then recently characterized fluorine monoxide.[43] This has been confirmed by later workers.[44,45] In a recent careful study of the vapour phase reaction of fluorine and water in a continuous system, however, ozone has been identified among the products.[46] In this work, excess of fluorine was used, with nitrogen as diluent, and at room temperature the reaction was slow, being incomplete in ten seconds; hydrogen fluoride, oxygen, ozone and hydrogen peroxide were identified among the reaction products, and there were also other unidentified oxidizing constituents. The reaction appeared to take place in two steps, the first rapid, the second slow.

In his study of the action of fluorine on aqueous solutions, Fichter was at pains to show that, in general, anodic electrochemical processes in aqueous solution could be duplicated by purely chemical processes, and to dispel any idea that there was something mysterious in electrochemical oxidations 'there still survives a remnant of the electrochemical mysticism which attributes to electrodes and to ions forces inaccessible to the ordinary chemist'.[18] 'With the right potential we can produce any effect of oxidation or reduction, regardless of whether this potential is attained by means of electrical voltage or by certain chemical reagents.'[19] Using fluorine, which because of its high electrode potential should be capable of achieving as much as the most powerful electrochemical process, these ideas were developed in a series of general papers[20] and particular contributions[17, 21-40] and there was also a contribution by N. C. Jones.[47] Whilst the general idea would be accepted without question, the method of oxidizing aqueous solutions with fluorine does not make any considerable contribution to knowledge, except to show that the oxidizing action is powerful. The reactions are complex, there are many side reactions and by-products, and these were never fully explored. Fichter failed to identify fluorine monoxide, which was first characterized when he was doing this work, and must have been formed in at least some of his reactions.

In general, the treatment of aqueous solutions with fluorine produces per-acids and the higher valency compounds of metals, as well as hydrofluoric acid. A good deal of attention was paid to the behaviour of bisulphate solutions. Potassium persulphate was separated and identified,[21] [22] and also ammonium persulphate.[23] Dry potassium bisulphate gave persulphate, but fluorosulphonate was also formed; potassium sulphate on the other hand, in the absence of hydrogen fluoride, showed no reaction.[24] Further study showed that there was a more powerful oxidizing agent present[25] and it was found that whilst at higher temperatures (above 40°C.) the reaction could be written:-

$$2KHSO_4 \rightarrow K_2S_2O_8 + 2HF$$

at lower temperatures the reaction took a different course:-

$$H_2SO_4 + F_2 \rightarrow SO_4 + 2HF$$

Studying a range of acid concentrations from 0·5 to 18·5 molar, it was found that the maximum production of the new oxide was obtained in 2 – 3 molar acid: at high acid concentrations there was very little action. The sulphur tetroxide is unstable, and is identical with that produced by reaction between ozone and sulphur dioxide:[24,35] it is also obtained from sulphate and bisulphate solutions at temperatures attained by ice–salt mixtures.

The treatment of chlorate solutions with fluorine gave perchlorates, and perchlorates gave hydrogen peroxide, the reaction being explained by the formation of per-perchloric acid, $HClO_5$.[32] In appropriate conditions potassium iodate was converted by fluorine into periodate.[38] Sodium nitrite is oxidized to nitrate, and nitrate to unstable pernitrates;[32] ammonium hydroxide and carbonate gave a complex range of compounds including nitric acids (in major proportions), nitrous oxide, nitrous acid, nitrogen and hydrazine.[39] The treatment of ammonia solution with fluorine was more difficult, owing to the resultant flames and explosions; here nitrate ion was missing, the major yield being nitrite ion and nitrogen, with some hydrogen, but not much nitrous oxide. Phosphoric acid in the cold gave the peroxy-acids H_3PO_5 and $H_4P_2O_8$ and alkali phosphates gave salts of these acids.[29] Borates gave perborates and carbonates gave percarbonates.[30] The treatment of acetate solutions with fluorine is likened to Kolbe's reaction; sodium acetate gave an explosive reaction involving the formation of diacetyl peroxide and its decomposition to ethane and carbon dioxide.[26] Later, potassium acetate solutions containing potassium carbonate were shown to give methyl alcohol and formaldehyde, the propionate similarly giving ethyl alcohol, formaldehyde, and ethylene.[33] It was possible, using fluorine, to prepare pertitanic, pervanadic and permolybdic acids, although here, as in many other cases, the ozone which is also formed reduces the per-acids so that yields are low.[37] Solutions of cerous salts were oxidized to ceric salts,[38] and similarly stannic, ferric, cobaltic,[26] and thallic salts were formed from salts of lower valency.[21]

From copper salts Cu_2O_3 was obtained while lead salts in alkaline solution were oxidized to plumbates.[31] Cobaltic sulphate crystals were obtained from solutions of cobaltous sulphate, and a solution of cobaltous carbonate in hydrofluoric acid gave a green solution said to be cobaltic fluoride.[27] Cobaltic perchlorate was also made from cobaltous perchlorate.[36] With fluorine silver salts gave black crystalline precipitates of a silver peroxide: the nitrate, sulphate, perchlorate and fluoride were investigated and the best yields were obtained from the nitrate in 3N. solution, which gave a compound $2Ag_3O_4,AgNO_3$. From chrome alum potassium dichromate was formed, and a suspension of manganous fluoride gave a red solution from which, by adding saturated potassium chloride solution, the crystalline salt K_2MnF_5,H_2O was obtained, though there was no indication of the formation of manganese tetrafluoride.[40]

Fichter[17] found that when fluorine acts on strong caustic potash in the cold, an ozonate, formulated as $(KOH)_2O_2$, is formed. He failed to observe the formation of fluorine oxide which was discovered a little later (see below). Fluorine oxide has no acidic properties, but Dennis and Rochow reported[41] that after fluorine was passed into 50% caustic potash at -40° there was an oxidizing agent present in the solution which could not be ozone or hydrogen peroxide, and was thought to be a hypofluorite. By electrolysis of potassium hydroxide-fluoride mixtures they claimed also to have isolated a fluorate. Cady, however, suggested that these observations could be attributed to the presence of chlorine, a very likely impurity in the material used,[42] and as this suggestion has not been rebutted, it may be regarded as the likeliest explanation. Thus it may be said that whilst Fichter's report about the formation of potassium ozonate may merit re-examination, there is no evidence for the existence of any fluorine oxy-salts of the character of hypofluorites or fluorates.

At least three compounds of fluorine and oxygen appear to exist. Lebeau and Damiens in 1927 observed the presence of a compound which proved to be fluorine monoxide[48] – which might better, it was suggested, be called oxygen fluoride,[49] – in the gases from a medium temperature cell when there was a little water in the electrolyte. Fluorine monoxide is a colourless gas; m.p. -223·8°C., b.p. -146·5°. A little later they described how the same compound was made by the reaction of fluorine with 2% caustic soda,[50] and this has become the usual method of production. In 1933 Ruff and Menzel described the action of an electric (glow) discharge on an equimolecular mixture of fluorine and oxygen at reduced pressures (30 – 40 mm.) and liquid air temperature. A difluorine dioxide, F_2O_2, was produced[51] as a yellow solid, melting at -160° to a red liquid boiling at -57° to a brown vapour which dissociates to a colourless gas. This dissociation was first reported to give rise to a monoxide, FO, but later it was shown that only fluorine and and oxygen were formed; there was no evidence for the existence of a compound of formula FO.[52] A third oxide, difluorine trioxide, is reported to be formed when a liquid mixture of fluorine and oxygen is irradiated with ultraviolet light.[53] The same workers showed that liquid mixtures of fluorine monoxide and oxygen, under the influence of ultra-violet irradiation, gave both the other oxides and that a silent discharge in fluorine gas, in the presence of liquid oxygen, also gave rise to F_2O_2 and F_2O_3.[54]

The reaction of fluorine with sulphur leads not only to the remarkably stable and inert sulphur hexafluoride, SF_6, but also to a mixture of lower fluorides if the fluorine supply is restricted. Disulphur decafluoride, S_2F_{10}, a liquid boiling at 29°C., was isolated in 1934.[55] It is very stable, but more reactive than sulphur hexafluoride, since although unaffected by aqueous potash it is attacked by alcoholic potash. By the action of fluorine on methyl mercaptan, (diluted with nitrogen, at 250°C.) trifluoromethyl sulphur pentafluoride, CF_3,SF_5, b.p. -20°C., and difluoromethyl sulphur pentafluoride, CHF_2,SF_5, b.p. 5·1°C., are obtained.[56] The former is also obtained on fluorination, by cobalt trifluoride, of methyl mercaptan or of carbon disulphide; it is stable to aqueous alkali, whilst the difluoro-compound is completely hydrolysed by 6N-caustic soda solution. The lower fluorides, SF_4, SF_2, and S_2F_2, have not been well characterised: besides being obtained as a complex mixture from the action of fluorine on sulphur,[57,58] they have been made by reaction of sulphur with fluorides, (*e.g.* sulphur tetrafluoride from sulphur and cobalt trifluoride,[59] disulphur difluoride from sulphur and silver or mercurous fluoride[60]) as well as by fluorination of other sulphur halides.[57] These compounds, gases boiling between -40° and -100°C., are unstable and are readily hydrolyzed by water.

Sulphuryl fluoride and thionyl fluoride have been known for many years, but mixed fluoro-chlorides and other fluoro-halides have been made more recently.[61,62] The action of fluorine on sulphur dioxide leads to sulphuryl fluoride, but can also give rise to sulphur hexafluoride, and to a new compound, SOF_4[63] which is also obtained by the action of fluorine on thionyl fluoride. It has been seen above that concentrated sulphuric acid shows little or no reaction with fluorine at room temperature.

Little has been added to the knowledge of selenium and tellurium fluorides gained by Moissan and his school, and by Prideaux. Selenium tetrafluoride has been made, with the hexafluoride, by the action of fluorine on grey selenium, as well as from selenium dioxide and chlorine trifluoride, a reaction which also gives rise to selenium oxyfluoride, $SeOF_2$.[44]

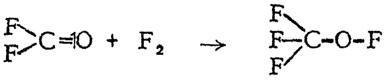
The development in knowledge of fluorine derivatives of the halogens is even greater than with the sulphur compounds. It is remarkable that Mellor, in the original book, was able to report that Ruff and Zedner obtained no result by heating fluorine and chlorine at the temperature of the electric arc, as the principal developments in this field have later come from Ruff and his school. The formation of a chlorine fluoride on passing hydrogen chloride gas into liquid fluorine was first observed in 1929.[64] It was then found that by passing fluorine and chlorine into a copper vessel at 250°C., chlorine monofluoride, ClF, could be obtained as an almost colourless gas condensing at -103° and having reactions very similar to those of fluorine itself. It was found that chlorine and fluorine would unite with inflammation[65] and in the correct proportions gave a violent explosion on sparking.[66] Later it was found that another compound, chlorine trifluoride, was obtained by heating fluorine and chlorine in proportion of three to one, to about 250°C.[67] This compound is a liquid, boiling at 12°C., which again reacts very much like fluorine; associates slightly at ordinary temperatures to a dimeric form,[68] and dissociates on heating to chlorine monofluoride and fluorine.[69] Bromine trifluoride was discovered almost simultaneously by Lebeau and by Prideaux, in 1906, but Ruff was able to show, in 1931, that further reaction occurred between the trifluoride and fluorine to give bromine pentafluoride, b.p. 40°C., which is also produced directly by interaction of bromine and fluorine in the correct proportions.[70] Bromine monofluoride, b.p. 20°C., is formed when equimolecular proportions of bromine and fluorine react, or preferably when excess of bromine reacts with the trifluoride or pentafluoride.[71] This compound very readily disproportionates into bromine and higher fluorides, and all the bromine fluorides are, like the chlorine fluorides, very vigorous fluorinating agents. The chemistry of solutions in bromine trifluoride, an ionizing solvent, has been actively studied by Emeleus and his school (see below). Iodine pentafluoride reacts with further fluorine to give the heptafluoride, which sublimes at 4·5°C.[72] and in fact is found to occur in the pentafluoride as normally prepared.

A new class of oxyfluorides has also quite recently been discovered.

Reaction between chlorine dioxide and fluorine is explosive but when they are mixed with a large excess of air a controlled reaction occurs giving rise to chlorine dioxymonofluoride, ClO_2F, b.p. -6°.[73] The controlled reaction of fluorine with concentrated perchloric acid gives ClO_4F, which was named fluorine perchlorate, other products, including fluorine monoxide, being also formed. This compound boils at -16°, and is highly reactive.[74] The corresponding iodine compound, IO_4F, could not be prepared, but the action of fluorine on periodic acid gives rise to many products, including oxygen fluoride and iodine pentafluoride.[75] Reaction of fluorine containing oxygen with iodine, or partial hydrolysis of iodine pentafluoride, or addition of iodine pentoxide to the pentafluoride, produces the compound IOF_3,[76] m.p. 9·6°C., b.p. 98°.[77] A compound of the formula ClO_3F is said to be formed by the action of fluorine on chlorates.[78]

Mellor referred to the failure to obtain nitrogen-fluorine compounds, and mentioned the formation of a nitryl fluoride, NO_2F, b.p. above 80°. This identification must have been erroneous, for no compounds of this type have so high a boiling point. Ruff says Moissan's results here prove to be 'not quite right'.[79] Whilst no reaction between nitrogen and fluorine has been reported, nitrogen trifluoride, b.p. -129°, has been obtained by the action of fluorine on ammonia[80] although only in low yield. This compound was, however, first made by Ruff, in 1928, by electrolyzing fused ammonium bifluoride at 125°, using a graphite anode.[81] The preparation is difficult, and there are many by-products, including, it is suggested, mono- and difluoroamine, NH_2F and NHF_2, which however were not isolated or characterized. This is an interesting early example of electrolytic fluorination, a process which, as applied to carbon compounds, has been developed by Simons.[82] It should be noted that by this process a whole series of fluorine-substituted primary and secondary amines, containing the groups $-NF_2$ and $>NF$, have been prepared. All these compounds are stable and inert; the fluorine is not hydrolyzable. By the action of fluorine on silver cyanide,[83] or on cyanogen,[44] compounds such as $CF{:}NF_2$ and polymers of this, and also $CF_3.NF_2$, have been prepared. By the action of fluorine, diluted with nitrogen, on hydrazoic acid, fluorine azide has been prepared.[84] This interesting compound, a greenish yellow gas, b.p. -82°, is extremely unstable, and very easily decomposes explosively. It decomposes slowly into difluoro-diazine, F-N=N-F, a stable colourless gas condensing to a solid at about -100°C. This compound is not hydrolyzed by water. There was a suggestion that a solid, obtained in small yield in the decomposition of fluorine azide, might be trifluoro*cyclo*triazine. Tetrafluorohydrazine, N_2F_4, has not been reported, but it may be expected to be a moderately stable compound.

Among the oxyfluorides of nitrogen, nitrosyl fluoride and nitryl fluoride, NOF and NO_2F, are readily made by the action of fluorine on nitric oxide and nitrogen dioxide respectively.[79] The reaction proceeds smoothly at temperatures just above the melting points of the oxides.[85] Fluorine gas in small concentrations (0·5%) is reported to inhibit the formation of nitric oxide when air is submitted to the electric arc or silent discharge.[86] The fluorination of concentrated nitric acid produces fluorine nitrate, NO_3F.[87] It may be noted that the boiling point of nitryl fluoride, -72·4°, is lower than that of nitrosyl fluoride, -60°, whilst fluorine nitrate boils at a rather higher temperature -46°. These compounds are hydrolyzed by water. The formation of fluorine perchlorate, of fluorine nitrate, and, as will be seen below, of the compound $CF_3.OF$ (by the action of fluorine on fluorophosgene) indicates the stability of the -O-F linkage, which is much greater than that of the corresponding -O-Cl linkage; it can hardly be called by analogy a hypofluorite, although the compound CF_3OF was named trifluoromethyl hypofluorite by its discoverers. The formation of this compound by addition of fluorine to ketonic oxygen,[88]



is curiously similar to the hydrogen reduction of such a bond. These reactions may be more general than these few cases indicate.

The reaction of fluorine with non-metallic elements other than carbon has been little studied. An attempt was made to determine the minimum fluorine concentration required to start rapid combustion of red phosphorus but very variable figures were obtained.[89] Some interest has been taken commercially in fluorophosphoric acids in recent years[90] and also in applications of boron trifluoride and its derivatives.

Developments in the carbon-fluorine field have been very considerable: there was indeed little to be said on this subject in the original work and many statements then made have proved to be in error. Any variety of carbon only becomes incandescent in fluorine because of its content of impurities, of hydrocarbons, or of moisture, etc. When thoroughly calcined to drive off combined hydrogen and adsorbed moisture, carbon does not react with pure fluorine at ordinary temperatures. The formation of carbon monofluoride, of tetracarbon monofluoride, and of 'graphite bifluoride', has been referred to above under the Preparation of Fluorine and will be dealt with in more detail later. At temperatures below 500°C. only these solid intercalation compounds are formed, but about this temperature a mixed reaction occurs; carbon monofluoride may be an intermediate compound, but tends to decompose to gaseous fluorocarbons as the temperature approaches 500°C. In these circumstances, and in presence of excess of fluorine, the conditions exist for a very rapid reaction to convert all the carbon to gaseous fluorocarbons, and this may proceed with explosive violence. Hence explosions often occur when fluorine reacts with carbon at temperatures a little above 500°C. At higher temperatures the reaction proceeds smoothly to form not only carbon tetrafluoride but also diminishing quantities of higher fluorocarbons, i.e. compounds of carbon and fluorine analogous to saturated hydrocarbons. The first fluorocarbons were made in this way, but a more extensive range has been produced by fluorination of hydrocarbons, either with elementary fluorine directly, or by solid active fluorine carriers such as cobalt trifluoride, or by electrolytic fluorination. Indirect means have also been employed, such as replacement of other halogens by reaction with hydrogen fluoride or other fluorine exchange reagents, especially antimony fluorides. In the latter case it is rarely that a pure fluorocarbon is obtained, the product is more usually a 'mixed' compound, such as difluorodichloromethane, or benzotrifluoride, or difluorochloromethane, which on pyrolysis gives tetrafluoroethylene, which on polymerization gives a polymer having remarkable properties. It is clear that parallel to the hydrocarbons there exists an equally large number of fluorocarbons, and parallel to the field of organic compounds there exists a field of compounds based on fluorocarbon skeletons. Although organic chemistry is often defined as the chemistry of the compounds of carbon, it may be doubted whether it is proper to include in organic chemistry the field of what may be called 'fluorocarbon chemistry', many though the contacts may be. Fluorocarbons and their derivatives are therefore here dealt with in a separate section.

Turning now to the reactions of fluorine with metals and metal compounds, the general behaviour of common constructional materials has been considered in the section on fluorine preparation, especially with regard to materials particularly suited for use with fluorine at temperatures above the ordinary (see page 62). There is no great difficulty in finding metals reasonably resistant to fluorine, although all metals will react at sufficiently high temperatures, even in massive form, and at lower temperatures when the metal is sufficiently finely divided. Thus Japanese workers have said that platinum, gold, magnesium, nickel, copper and monel metal show good resistance to fluorine, as also does bakelite.[91] There have been many contributions, mainly by American authors, since the war, on the resistance of materials to fluorine, as well as information, given incidentally, in accounts of fluorine production already referred to. Table VIII gives quantitative measurements of the corrosion rate of some more resistant metals at elevated temperatures.

TABLE VIII— CORROSION RATES IN FLUORINE PENETRATION, IN THOUSANDTHS OF AN INCH PER MONTH

Metal	Temperature, °C.		
	500°	600°	700°
Nickel	5·1 (6)	29 —	34 (100)
Monel (70:30 Ni:Cu)	2 (20)	60	150 (200)
Inconel (18:14:6 Ni:Cr:Fe)	62	170	510
Copper, deoxidised	120 (200)	990	2900 (3000)
Aluminium, commerically pure	13 (40)	18 (60)	

The upper figures are given by Landau and Rosen;[92] the lower figures in parentheses given by Myres and DeLong[93] are generally in agreement.

TABLE IX— CORROSION RATES IN FLUORINE PENETRATION, IN INCHES PER MONTH

Metal	Temperature, °C.		
	300°	400°	500°
Armco iron (pure iron)	0·009	0·024	11·6 (11)
Sheet steel (Si—trace)	0·009	0·015	19·8
(Si—0·07%)	0·66	0·012	7·4
(Si—0·007%)	0·83		
(Si—0·18%)	0·75		
(Si—0·22%)	0·66	0·54	
Music wire (Si—0·13%)	0·40		
Stainless steels %Cr %Ni			
14–18 —	0·255	0·078	
18 10	0·213	0·795	
25 12	0·075	0·665	
25 20	0·031	0·561	

Table IX gives corrosion rates of ferrous alloys at lower temperatures reported by the same authors. It is suggested that low silicon content contributes to the corrosion resistance of steels: the slight influence of chromium and the beneficial influence of nickel are to be noted. The corrosion of magnesium alloy (10% Al) was negligible up to 300°C.[93] The uses of aluminium and magnesium alloys are likely to be restricted rather by inadequacy of mechanical properties at higher temperatures, than by any loss of corrosion resistance. In anhydrous hydrogen fluoride, corrosion rates, except for aluminium, were very much less: for nickel the rate was only one tenth of the above, and copper, monel and inconel gave similar figures: the corrosion of ferrous materials was also much less.[93]

Landau and Rosen also referred to the high resistance of β-alumina, and of calcium fluoride cement.[92] In other contributions, authors recognize the high value of nickel and nickel-copper alloys, and of steel at temperatures up to 250°C. Lead is not very satisfactory, and stainless steel, which shows pitting, is to be avoided.[94] Tantalum reacts with fluorine and is not recommended.[95] This presumably must be related to the high volatility of tantalum pentafluoride, as the corrosion resistance of other metals is usually attributed to the formation of fluoride films. For the same reason – volatility of the corrosion product – platinum is unsatisfactory for high temperature work.[96] In equipment for handling fluorine under high pressure nickel is mainly used,[97] though steel cylinders are used for its transport at 400 lb./sq.in.[98]

Though reference has been made (see page 15) to one case in which it is claimed that oxygen will displace fluorine, fluorine will in general tend to displace all other non-metallic elements from their compounds. The ease with which this displacement occurs, however, varies appreciably. With halides, the displacement occurs readily and at ordinary temperatures or a little higher, as will be seen in examples below. With oxides the displacement does not occur nearly so readily, a fact related, perhaps, to the lower energy of chlorine, bromine and iodine bonds as compared with oxygen bonds, though another factor must be the readiness with which all the halogens form compounds with fluorine, having positive heats of formation, thus tending to reduce the equilibrium pressure of halogen X in the general reaction,

$$2MX + F_2 \rightarrow 2MF + X_2$$

and so increase the tendency for the reaction to proceed. Thus, as an example of the resistance of oxides to attack, the value of alumina in vessels for handling fluorine at high temperatures has been stressed: yet we can write

$$Al_2O_3 + 3F_2 \rightarrow 2AlF_3 + 1{\cdot}5\ O_2 + 237\,\text{kg.-cal.}$$

Glasses also, though attacked by hydrogen fluoride, are less readily attacked by fluorine, and Rudge reports that provided stringent precautions have been taken to remove hydrogen fluoride, soft soda glass may be heated in fluorine to at least 150°, borosilicate glass to 200°, and silica to 250°, without any visible sign of corrosion occurring; and that these materials are quite usable for limited periods at appreciably higher temperatures if a certain amount of etching can be tolerated.[96] Oxysalts vary in their susceptibility to attack; it has already been seen that potassium nitrate is attacked to give fluorine nitrate – and presumably potassium fluoride – and that potassium bisulphate is attacked whilst the sulphate is not. In general, as might be expected, lower fluorides are converted into higher fluorides by the action of fluorine.

The action of fluorine on alkali metal halides has been proposed as a ready means of determining fluorine in connection with current efficiency measurements, and using potassium chloride or calcium chloride this action may serve also to dispose of unwanted fluorine, the displaced chlorine being absorbed *e.g.* in caustic soda.[92] Only recently has any attention been paid to the solid product formed by the action of fluorine on alkali fluorides.[78] With potassium, rubidium or cæsium chloride as starting material, the fluoride first formed is pseudomorphic with the chloride, and further fluorine can readily be taken up by this pseudomorph giving higher compounds; potassium giving KF_2, cæsium CsF_3, and rubidium either RbF_2 or RbF_3. These compounds are diamagnetic and strongly oxidising, but the cæsium compound does not decompose below 300°C. Mixtures of an alkali halide and anhydrous nickel chloride give compounds of the type $M_2(NiF_6)$. Mixtures of alkali halides and, *e.g.*, antimony oxide give more stable perfluorides. Interest was aroused in 1933 when the new argentic fluoride AgF_2 was reported to be obtained by the action of fluorine on silver.[99] The discovery was quickly confirmed by a disappointed man who had made the compound and failed to identify it.[100] Ruff showed that fluorine attacks silver halides to give the difluoride.[101] The same compound was also obtained from silver oxide and fluorine.[102] Silver cyanide reacts with pure fluorine at ordinary temperatures with explosive violence, but by reducing the concentration of fluorine (by reducing the pressure) and diluting the cyanide with fluorspar, the reaction can be controlled, and compounds of fluorine with nitrogen and carbon are obtained as well as silver difluoride.[83] The fluorination of a molten mixture of silver mono- and difluoride, or of molten mixtures of silver fluoride with the fluoride of mercury, cobalt or manganese, for use in making fluorocarbons, has been patented,[103] as has also the use of silver difluoride for liquid or vapour phase fluorinations.[104] The action of fluorine on copper does not give any higher fluoride than the cupric salt, CuF_2:[101] Ruff commented that even with finely divided copper, the stability to fluorine is noteworthy even up to 350°C. A little chlorine added to the fluorine accelerates the reaction greatly. On massive copper a layer of white cupric fluoride is formed over cuprous fluoride. At red heat, cupric fluoride is volatile, and although Moissan thought that the vapour reacts with fluorine to give a perfluoride, it was not possible to confirm this even up to 680° in the calcium fluoride vessel used.[101] A mixture of potassium chloride and cupric chloride in molecular proportion of 3 : 1 when gently heated in fluorine gives a green compound having the formula K_3CuF_6;[105] this is evidently comparable with the alkali metal perfluorides referred to above. Mercury reacts with fluorine, and this reaction has been used in the analysis of fluorine from cells (see page 17). Mercuric cyanide when gently heated reacts vigorously with fluorine, burning with a flame[83] mainly to form carbon tetrafluoride, nitrogen and mercuric fluoride.

The resistance of aluminium oxide to attack by fluorine has already been described. Ruff, in contrasting the attack on aluminium by chlorine monofluorine and by fluorine, says that aluminium burns more rapidly in the former, but does not state the conditions.[65] The fluorides of gallium, indium and thallium have been made with fluorine.[106] Gallium oxide reacted, sometimes at room temperature, more usually at about 200°C., but the reaction was incomplete, and even at 600 – 650°, some 5% of oxide remained unchanged. The hydroxide behaved similarly, and the sulphide was not greatly attacked. The chloride does not seem to have been tried, but the preferred method of preparation was to precipitate ammonium gallium fluoride, $(NH_4)_3GaF_6$, and calcine it in a stream of fluorine. Indium fluoride was readily made on gently warming the oxide in fluorine, but it was necessary to heat to 500° for several hours to complete the reaction; the route *via* ammonium indium fluoride was also used. The reaction of thallium oxide with fluorine began at room temperature and was completed on gentle heating. Thallous chloride reacted violently with fluorine and the product melted.

Lead difluoride reacts so vigorously with fluorine at 250°C. that the product is fused and the reaction is incomplete, but by diluting the fluorine with an equal volume of carbon dioxide, the reaction can be controlled.[1] Evidence that the difluoride has but a small partial pressure of fluorine at 600°C. was confirmed by an estimate of the heat of reaction:-

$$PbF_2 + F_2 \rightarrow PbF_4 + 63 \text{ kg.-cal.}$$

Though the question whether lead tetrafluoride can give fluorine by thermal dissociation has been discussed earlier under 'Preparation', it may here be noted that the production of lead tetrafluoride has been described, and its use in the fluorination of organic compounds claimed, in a series of patents.[107] The reaction of cerium oxide with fluorine does not readily go to completion, and some oxygen is retained, but cerium trichloride reacts at room temperature with fluorine, and the final product is the tetrafluoride, CeF_4.[106,108] This product was believed to be pseudomorphous with the chloride, because of the low density.[108] It was not possible to prepare tetrafluorides of praseodymium or neodymium in a similar manner. The production of cerium tetrafluoride by the action of fluorine on the trifluoride (obtained by reaction between the trichloride and hydrogen fluoride) and the use of the tetrafluoride as a fluorinating agent for organic compounds have been patented.[109] Bismuth pentafluoride has been made from the trifluoride and fluorine.[1]

Considering the elements of Group VI, the fluorides of uranium are of special interest and importance. The fact that the hexafluoride was the only compound of uranium volatile at a reasonable temperature led to its use in the diffusion process for separating $U^{235}F_6$ from $U^{238}F_6$, and because it, like many higher fluorides, was a powerful fluorinating agent, there arose a demand for fluorocarbons for the wartime Manhattan Project. The production of the hexafluoride from fluorine and uranium tetrafluoride as well as by other reactions such as the action of fluorine on uranium oxide or uranyl fluoride has been described.[110] In Germany it has been made by the action of fluorine on uranium oxide, U_3O_8.[63,111] Whilst molybdenum, tungsten and uranium form hexafluorides, as do sulphur, selenium and tellurium, no chromium hexafluoride has been prepared. Von Wartenberg found that the highest fluoride obtained in the fluorination of chromic chloride or fluoride, $CrCl_3$ or CrF_3, was a pentafluoride. A tetrafluoride was readily obtained also, especially when finely divided metal was fluorinated; though from the metal it was not possible to obtain the pentafluoride. From chromic acid, CrO_3, in a stream of fluorine at 50 – 100°C., some pentafluoride was obtained, whilst chromyl chloride and fluorine readily gave chromyl fluoride, even with a flame at appropriate concentrations.[112] It is noteworthy that in the production of fluorides by an autoclave reaction between chlorine trifluoride and metals, chromium does not readily react.[44] Certain anomalous results in an attempt to determine the electron affinity of fluorine by heating a tungsten filament in fluorine were explained by suggesting that a very stable adsorbed layer of fluorine on tungsten was retained even at 2600°K.[113] Rhenium readily reacts with fluorine at 125°C. to give the hexafluoride, ReF_6;[114] while rhenium oxide and potassium per-rhenate yield two oxyfluorides, $ReOF_5$ and ReO_2F_3.[115] Manganese oxides, MnO and Mn_3O_4, react with fluorine and even when this gas is diluted with nitrogen the reaction is vigorous below 100°C., giving rise to manganese trifluoride, MnF_3; and potassium permanganate reacts at 150° to give the same product.[115] This is the highest fluoride of manganese which has been reported, and thus the behaviour of manganese, like that of chromium, is anomalous in that these elements do not exhibit their highest valency in their fluorides. The decomposition of manganese trifluoride has already been reviewed (see page 16); the production of the trifluoride from the difluoride and fluorine and its use in fluorination of organic compounds have been described in patents.[104,116]

Ferric chloride reacts with fluorine to give a mixture of ferric and ferrous fluorides[117] and when the salt is mixed with potassium chloride it yields only K_3FeF_6 and no higher fluoride.[105] Cobaltic fluoride has aroused much interest, especially with regard to the possibility of obtaining fluorine from it by heating (see page 16). It is readily obtained from the difluoride or dichloride and fluorine,[17] and gives up one atom of fluorine to reducing substances; e.g. when mixed with sulphur it gives the lower fluorides of sulphur[59] and on gently warming a mixture of cobaltic fluoride with silicon, the whole mass glows red.[65] Its use as a fluorinating agent for organic compounds has been patented.[104,118]

A mixture of potassium chloride (3 mol.) and cobalt chloride (1 mol.)

when gently heated in fluorine gives a blue salt K_3CoF_7.[105] Nickel chloride and potassium chloride, mixed in the molecular proportion 1 : 2, give in the same circumstances the red salt K_2NiF_6, but nickel chloride and fluorine alone give only the salt of bivalent nickel, NiF_2. There is little evidence for the existence of higher nickel fluorides, but it has been reported that the salt K_2NiF_5 occurs in the sludge of fluorine cells using nickel anodes.[119] Among the fluorides of the noble metals[65,117] rhodium trifluoride is obtained on gently heating the chloride in fluorine, and the higher fluorides RhF_4 and RhF_5 are produced on heating the metal or its chloride or fluoride in fluorine at 500°; palladous chloride with fluorine gives the trifluoride. Reference has already been made to the formation and decomposition of platinum tetrafluoride (see page 16) and the formation of this compound at temperatures of the order of 400°C. has been seen to limit the value of platinum for use in fluorine (see page 17). Iridium hexafluoride, IrF_6, is obtained on heating powdered iridium in fluorine at 260°C.[120]

Arising from a suggestion that combination of argon and krypton with both chlorine and bromine had been observed under the influence of an electric discharge on the mixed gases, similar experiments were made with fluorine and the inert gases. Ruff and Menzel[121] failed to find any evidence of compound formation, but von Antropoff, author of the original observations, considering that the conditions differed from those in his experiments[122] expressed an intention to repeat the experiments with fluorine. There has, however, been no further report, and it may be concluded that no evidence of compound formation has been obtained.

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THE ADDITIVE PROPERTIES OF FLUORINE AND ITS COMPOUNDS

The substitution in organic compounds of hydrogen or chlorine by fluorine, particularly poly-substitution, usually brings about remarkable changes in the properties, both physical and chemical. In consequence, many investigations of the physical properties of fluorine compounds have been made, especially with the object of discovering general relationships between properties and constitution.

The contribution of the fluorine atom to the molecular volume in its compounds is given as 9–10 cc.[1] Consideration[2] of the data for boron trifluoride and iridium hexafluoride according to van Laar's theory of the equation of state of gases and liquids, leads to values for the fluorine atom in b_0 and $\sqrt{a_0}$ of 31×10^{-5} and $2{\cdot}0 \times 10^{-2}$ respectively.

Allen and Sugden[3] deduced 25 for the parachor equivalent of fluorine but Desreux[4] showed that the value varied according to the type of compound, *e.g.* aliphatic or aromatic, mono- or poly-substituted, from whose properties it was derived. More recently, Vogel *et al.*,[5] using a system of bond, instead of atom, equivalents, gave a preliminary value of 28·2 for the C–F bond. Consideration has also been given[6] to the atomic contribution of fluorine to the thermochor, a modified parachor function given by $V^{5/6}\ T^{1/4}$, where V is the molecular volume at the boiling point, T.

Swarts[7] assigned 0·97 to the atomic refraction of fluorine for the $\mathrm{Na_D}$ line but pointed out that the value varied with the type of compound, as was also found by later investigators.[8] The method of derivation of an average value of 0·997, deduced[9] from measurements on 30 liquid aromatic fluorine compounds, was criticized.[10] Determination in recent years of the refractive indices of a large number of fluorine compounds, mostly poly-substituted, has established that the atomic refraction of fluorine increases markedly with the degree of substitution. The currently accepted values[11] are as follows:-

No. of F atoms/molecule	1	2	3	4	5	Perfluoro-compounds
AR_F	0·95	0·99	1·02	1·08	1·14	1·23

Refractivity has also been treated[12] as additive of contributions due to electron groups, both shared and unshared, in the molecule. Using this system, the contributions of the following bonds involving fluorine have been given:-[13]

C–F, 1·60; S–F, 1·95; Se–F, 2·23; Te–F, 2·47.

Vogel *et al.*,[5] also using a system of bond equivalents, gave 1·44 for the refraction equivalent and 28·27 for the refraction coefficient of the C–F bond. These are preliminary values based on determinations for a few aliphatic and aromatic monofluorides.

Audsley and Goss,[14] using data derived from determinations of refractive index,[15] and dielectric constant,[16] found that the contribution of the fluorine atom to distortion polarization (P_{E+A}) in compounds of both the types RX and CX_4 was 0·9.

Pascal[17] gave the atomic magnetic susceptibility of fluorine as 63–64 × 10^{-7} while the magnetic rotativity, calculated from that of difluorodichloromethane, has been given as $0{\cdot}55 \times 10^{-5}$.[18]

It has been shown[19] that the function $b = M \log_{10} T + 8{\cdot}0\ \sqrt{M}$, where M is the molecular weight of a compound and T its boiling point (in°K), is additive, the contribution of F being given as 68; C, 23·2; H, 10·9; Cl, 121·0; etc. The function $\phi = 100\ \sqrt{M}/p_k$, where M is the molecular weight and p_k the critical

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pressure (in atm.), has also been found[20] to be additive, being given by 33 + Σ atomic contributions. The atomic contribution for F is 23; for H, 0; for C, 23; for Cl, 32; etc.

Turning now to the fluoride ion, considerable attention has been devoted to its thermochemical properties. The proton affinity, *i.e.* the heat of the reaction

$$H^+ \text{(gas)} + F^- \text{(gas)} \rightarrow HF \text{(gas)}$$

has been given as 361 – 368 kg.-cal.[21] The heat of hydration has been calculated[22] and found to be 118 kg.-cal./g. ion, relative to K^+ = 74 kg.-cal., and this value fits on the smooth curve obtained when the heats of hydration of univalent ions are plotted against the 'thermochemical radius' defined by Kapustinskii.[23] A 'crystallochemical electronegativity', alternative to Pauling's thermochemical electronegativity, has been proposed by this author.[24] This is derived from the lattice energies of solid crystalline salts, the energies of the gaseous ions being assumed to be additive. The crystallochemical electronegativity of the fluoride ion is fixed by convention as 1, examples of values for other ions being:-

H^-, 1·8; Na^+, 15·6; K^+, 14·8; Ca^{++}, 18·6; Cl^-, 2·1; Br^-, 2·3.

Kapustinskii's more refined method of calculating lattice energies has been shown[25] to offer no advantage over the simpler method. The standard entropy of the fluoride ion in the crystalline state has been calculated[26] and the value related to that of other ions according to the ionic charge and size.

The radius of the fluoride ion in solid crystals has been recalculated[27] from *X*-ray measurements and given as 1·13A. The volume of the fluoride ion has been estimated from the densities of fluorides at ordinary temperatures[28] and at their melting points.[29] The apparent volume of the fluoride ion at infinite dilution in aqueous solution has been estimated[30] to be – 1·8 c.c./equivalent, *i.e.* the hydrated ion occupies this much less space than the water of solvation when free. Attention has also been given to both the structural[31] and energetic aspects[32] of the hydration of the fluoride ion, while solvation in non-aqueous solvents such as alcohols, acetone, acetonitrile and benzonitrile has also been considered.[33] Of properties related to the size and solvation of the ion, the specific viscosity contribution of the fluoride ion in 0·1N. aqueous solution has been given[34] as 0·0162. The transference velocity of the fluoride ion in aqueous solution at 18°C. has been determined,[35] while the ionic mobilities of fluorine at infinite dilution in water and in methanol at 25°C. have been found[36] to be 54·4 and 40·2 ohms respectively.

Wasastjerna[37] calculated from his determinations of the refractive indices of fluoride solutions[38] a value of 2·20 for the refractivity contributions of the fluoride ion, though Fajans and Joos[39] gave a value of 2·5. The value of α/r^3, where α is the polarizability and r the radius of the fluoride ion, has been given[40] as 0·33 $\times 10^{-24}$ (Cl, 0·51; Br, 0·56; I, 0·62).

The magnetic susceptibility contribution, $\times 10^6$, of the 'gaseous' fluoride ion is given variously as 12·2,[41] 9·4,[42] 12,[43] and 9·2,[44] while in aqueous solution the value is given as 13·0.[43]

Some attention has been given to the colloidal properties of the fluoride ion. Freundlich[45] regarded it as being at the extreme end of the Hofmeister anion series as judged by its effects on the coagulation of sols, on surface properties and on the solubility of highly soluble substances. In its effect on the coagulation of various hydroxide sols, the fluoride ion behaves as a bivalent anion, F_2^{--}[46] A similar conclusion was reached from a study[47] of the properties of ferric oxide sols prepared in presence of sodium fluoride. The adsorption of fluoride ions by sugar charcoal from potassium fluoride and from hydrofluoric acid solutions has been studied[48] and compared with that of chloride ions from the corresponding chloride solutions.

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SECTION III.

THE PREPARATION OF HYDROFLUORIC ACID.

By H. R. LEECH

The nomenclature of chemistry grows by a constant series of compromises: on the one hand logical systems are proposed, whilst on the other hand the chemical worker, developing that familiarity which breeds contempt, frequently takes short cuts through the system. A case in point is the compound with which we must now concern ourselves. The pure compound is hydrogen fluoride: and its aqueous solution is hydrofluoric acid. But at what water content does the one become the other? The question is not academic; acid of 60% hydrogen fluoride content is an article of commerce. In making the anhydrous material, intermediate products contain 80%, 95%, and 99% of hydrogen fluoride; which of these grades ceases to deserve the name of acid? In many other cases, no distinction of this kind is drawn: thus in the case of sulphuric acid, for example, at no concentration is the name 'hydrogen sulphate' applied. The term hydrofluoric acid will therefore be used generally, and the compound will be described as 'anhydrous' when it is considered that the term is justified and that no confusion can arise. It may, perhaps, be pointed out that whilst Mellor acknowledged a distinction between 'hydrogen fluoride' and ' hydrofluoric acid' he generally uses the term 'anhydrous hydrofluoric acid'.

Whilst Mellor originally said that hydrogen fluoride rarely occurs free in nature, it is probable that this statement requires modification. The presence of this compound in volcanic exhalations and in fumaroles seems to be very general, as has already been remarked (see page 3), and the escape of hydrofluoric acid in this way is an integral part of the fluorine cycle in nature.

FORMATION OF HF

The reaction of fluorine with hydrogen to give hydrofluoric acid has already been considered (see page 54), as also has the reaction of fluorine with water (page 55). The reaction of fluorine, or of active fluorides such as cobalt trifluoride, with hydrocarbons, to give fluorocarbons, has been given much attention in recent years, and in this reaction hydrofluoric acid is a by-product (see page 198). The principal chemical process in which hydrofluoric acid is a by-product is the working up of phosphate rock, mainly to superphosphate. It has been shown that most rock phosphates used in the U.S.A., for example, contain 3 – 4% of combined fluorine, and that in treating them with sulphuric acid in the usual superphosphate process, a proportion of this, varying between 11 and 42%, is volatilized, the average being between 20 and 30%. This may escape partly as hydrogen fluoride, partly as silicon tetrafluoride, owing to the presence of siliceous impurities; and some of it is recovered as hydrofluosilicic acid. In furnace processes for phosphorus production, between 10 and 30% of the fluorine in the phosphate rock may be volatilized.[1]

The formation of hydrogen fluoride by the reaction of hydrogen with metal fluorides has been used as a preparative method, using silver fluoride, more particularly to make deuterium fluoride, (see page 86). The general reaction has been studied by Jellinek and Rudat.[2] The hydrogen fluoride content of hydrogen passed over a number of fluorides at various temperatures, and at various flow rates, was determined using a copper reactor; the results were extrapolated to give the hydrogen fluoride content at zero flow rate, which would be the equilibrium concentration.

The equilibrium content of hydrofluoric acid thus derived for different fluorides is given in Table I, as percentage by volume – all the experiments being at a total pressure of 1 atmosphere.

TABLE I. - REDUCTION OF FLUORIDES BY HYDROGEN.
EQUILIBRIUM PERCENTAGE OF HF AT DIFFERENT TEMPERATURES.

Temp. °C.	300	350	400	450	500	550	600	700	750	800
NiF_2	5·6		30·8		51·7	73·7				
FeF_3 (to FeF_2)		2·9		13·0		42·0				
CoF_2			9·9		33·7		78·0			
CdF_2			4·2		18·75		53·0			
CrF_3 (to CrF_2)			2·85		10·6		29·2			
FeF_2					4·7			21·3		
ZnF_2							6·8	20·3	32·3	
CrF_2							1·4	3·05		5·2
MnF_2							0·33	0·61		1·01

From the equilibrium constants calculated from these data, and a knowledge of the thermochemistry of hydrofluoric acid itself, it is possible to calculate the partial pressure of fluorine over these fluorides, when heated alone, owing to decomposition: the values are, of course, extremely small, ranging from 10^{-29} atm. over ZnF_2 at 800° to 10^{-53} atm. over CoF_2 at 300°C. From the slope of the $\log p - 1/T$ curves, the heats of formation of the fluorides were calculated. (Table III).

A somewhat similar series of experiments has been carried out on the reaction of a number of metal fluorides with water vapour[3], the water vapour flow rate being varied and equilibrium conditions calculated by extrapolation to zero flow.

The equilibrium concentrations of hydrofluoric acid are given in Table II, again for a total pressure of one atmosphere.

TABLE II. - REACTION OF FLUORIDES WITH WATER VAPOUR.
EQUILIBRIUM PERCENTAGE OF HF AT DIFFERENT TEMPERATURES.

Temp. °C.	200	300	350	400	450	500	550	600	650	700	750	800	900	1000	1100
AgF	3	12	20	41.5											
CuF_2		16	24.5	48.5											
FeF_2		12.5		25.5	36.5	46	56								
FeF_3		16	30.5	48.5	66										
ZnF_2				8.5		25	38	52.5	66						
CrF_3				17.5	28.5	42	56.5	70							
PbF_2						2.8		9.5	16.5	26	38				
MnF_2						4.5		10.5		17		24			
CoF_2						10		27	39.5	53		65.5			
NiF_2						14	24.5	38	53	67					
MgF_2													3.15	6.6	12
CaF_2													0.5	1.15	2.3
BaF_2													0.6	1.1	1.9

The heats of formation of the fluorides were calculated, and the results are given in Table III, together with the calorimetric values obtained by von Wartenberg, and the values calculated by Jellinek and Rudat from the hydrogen reduction, for comparison. The agreement in general is reasonably good.

TABLE III. - HEATS OF FORMATION OF FLUORIDES, kg.-cal.

In the table below, the second column gives the calculated value of the heat evolved in the steam reaction, the third the known heat of formation of the oxide, the fourth the value calculated from these for the heat of formation of the fluoride. The determined values, from von Wartenberg's work, are then given in the fifth column, and finally the values calculated in the work of Jellinek and Rudat on hydrogen reduction.

Compound	Steam Reaction	Oxide	Fluoride		
			calc.[1]	det'd.	calc.[2]
CuF_2	-25·2	37·2	131·8	140·4 aq.	
MgF_2	-44·3	146·1	259·8	264·3	
CaF_2	-48·5	151·4	269·3	289·4	
BaF_2	-37·25	134·04	240·7	277·9	
ZnF_2	-25·8	84·9	180·1	193·0 aq.	172·7
CdF_2	-28·45	65·2	163·0	173·7 aq.	162·2
PbF_2	-37·2	50·3	157·0	156·0	155·6
CrF_3	-65·6	266·0	270·35	(283·0+a)*aq.	230·9
FeF_3	-61·3	191·1	230·3	243·1 aq.	233·25
CoF_2	-29·85	57·5	156·75	172·8 aq.	160·7
NiF_2	-30·5	58·6	158·5	171·4 aq.	157·5

* a is the heat of hydration of Cr_2O_3, not known.

It is worth noting that this investigation was begun because in using fluorspar porcelain as described by Damiens, it was found to give a slightly alkaline reaction with water, reaction having occurred with atmospheric moisture. Copper fluoride was difficult to make by the action of fluorine on copper, even when the metal was finely divided and heated at 400°C. Copper carbonate was heated with anhydrous hydrofluoric acid at temperatures finally reaching 400°C. Silver fluoride was made by dissolving the carbonate in aqueous acid, evaporating to dryness in the dark, redissolving, filtering in platinum and evaporating again. On heating with steam, metallic silver was obtained, so that no useful result can be recorded. Manganous and ferrous fluorides, on the other hand, gave the sesquioxides, M_2O_3, and again the results were inapplicable.

PRODUCTION.

Both aqueous and anhydrous hydrofluoric acid can be purchased freely nowadays; the latter is contained in steel pressure cylinders as the compound must be treated as a liquefied gas.

A neat and simple method of making a small amount of aqueous acid in the laboratory has been described.[4] A piece of lead pipe is bent roughly to the shape of a retort, and the shorter limb is closed by hammering the end flat. The requisite amounts of fluorspar and sulphuric acid are then introduced through a paper cone and a filter funnel, and on heating the distillate is collected in a paraffin-wax coated glass bottle cooled in ice.

The preparation of hydrofluoric acid has been reviewed, and methods of purification of reagent quality acid described.[5]

The production of hydrofluoric acid on an industrial scale has undergone a revolution in the last thirty years. At the time when the original Treatise was written, aqueous hydrofluoric acid was made industrially on a not very considerable scale. The anhydrous acid was not available commercially, and when it was required in the laboratory it was made by heating Frémy's salt, which, as has already been seen, was a serious complication in making fluorine, so that the introduction of the high temperature cell in which Frémy's salt could be electrolyzed directly was a great advantage to those working in this field. When the medium temperature cell was introduced, a description was given of the making and storing, in a steel cylinder, of anhydrous acid, to be added to the cell as required. Reference has already been made to the first reported use of a commercial supply of anhydrous hydrofluoric acid in 1931 (see page 42), but the anhydrous acid was not made primarily for use in the fluorine cell, but for the production of fluorochloromethanes ('Freons'). The growth of the demand for this type of compound has led to a very considerable expansion of the industry producing anhydrous hydrofluoric acid, and this has been further assisted by increasing use of hydrofluoric acid as a 're-forming' catalyst in the petroleum industry, and by the demand for it by the expanding atomic energy industry. This growth has been most marked in the U.S.A., though the establishment of anhydrous hydrofluoric acid manufacture has been reported in Great Britain and in Germany. Some figures have been given for U.S. production up to 1944.[6] It is stated that the first production of anhydrous acid was 500 tons in 1931, the production of aqueous acid in 1933 was equivalent to 1358 tons, and in 1944 the estimated figures were: anhydrous acid 24,900 tons, aqueous acid 12,800 tons. The expansion of the latter is noteworthy, and is presumably related to the enormous increase in aluminium production, with the consequent demand for synthetic cryolite, and to the production of fluoride-containing fluxes for the light metal industry. An indication of the growth of this industry in the U.S.A. is given by the following figures for the total amount of fluorspar used in that country for hydrofluoric acid production:-[7]

Year	1930	1935	1940	1944	1945	1948
Fluorspar, tons	12,600	12,900	37,000	129,500	109,315	107,280

Except for hydrofluoric acid obtained as a by-product from mineral phosphates and the direct use of cryolite in the production of aluminium, all the fluorides and fluorine compounds of industry and commerce come from fluorspar, from which hydrofluoric acid is liberated by the action of sulphuric acid. It should perhaps be noted that hydrofluoric acid is liberated on the calcination of many fluorine-containing minerals, and it has been suggested *e.g.*, that in the calcination of an American topaz mineral to give a mullite refractory, the hydrofluoric acid evolved might be recovered.[8] Some attention will be paid later to the production of anhydrous acid by calcination of Frémy's salt (see page 81), but this of course is derived from fluorspar. There has been little work on the chemistry of the fluorspar–sulphuric acid reaction, beyond that described by Mellor. The heat evolved in the reaction $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$, calculated from the heat of formation of the constituents, using 96% sulphuric acid and producing liquid hydrogen fluoride, is negative to the extent of 7·3 kg.-cal. Mellor reported that calcium fluorosulphonate was present in the residue when the hydrofluoric acid had been distilled off, and that if the sulphuric acid used contained excess of sulphur trioxide, fluorosulphonic acid distilled with the hydrofluoric acid. It has been shown that fluorosulphonic acid is formed when strong sulphuric and anhydrous hydrofluoric acids are mixed.[9] Not unexpectedly, therefore, it has been demonstrated that fluorosulphonic acid is formed when calcium fluoride and sulphuric acid are mixed.[10] On mixing equimolecular proportions of 93·7% sulphuric acid and ground fluorspar, 15% of the acid forms fluorosulphonic acid: with 98% sulphuric acid, 20% forms fluorosulphonic acid. Using ground fluorspar the maximum formation of fluorosulphonic acid was observed at 35°C., but with precipitated calcium fluoride the conversion was greater and the maximum was at room temperatures. On heating, the equilibrium:-

$$H_2SO_4 + HF \rightleftharpoons HSO_3F + H_2O$$

is displaced to the left; and on removing hydrogen fluoride from the system the fluorosulphonic acid will be completely decomposed. The presence of sulphur trioxide on the other hand may be expected to favour the formation of fluorosulphonic acid, but the persistence of the calcium salt is not explained.

In the manufacture of hydrofluoric acid, the choice of raw material is important: the sulphuric acid should be of 98 – 99% strength,[6] and this will affect the water content of the product. A high grade fluorspar is required; the mined product may be contaminated with silica, which will give some silicon tetrafluoride or hydrofluosilicic acid in the product; and with sulphides, such as galena, which will reduce some sulphuric acid to sulphur dioxide. A hand picked grade was at one time suitable as 'acid spar', but the increase in demand has led to the application of beneficiation processes, usually a flotation operation, to the run-of-mine material containing, *e.g.* in one American case only 40 – 60% of calcium fluoride.[11] It is said that the fluorspar from certain Bavarian mines is of high purity, but a flotation plant was installed to ensure uniformity.[12] The product will be specified as having a minimum calcium fluoride content of 98·5% or 99%. It has been pointed out that the aqueous hydrofluoric acid and compounds prepared from it are frequently contaminated with traces of manganese.[13]

THE HYDROFLUORIC ACID INDUSTRY

In the original Treatise, Mellor described the manufacture of hydrofluoric acid in a cast iron retort with a cast iron cover. From these retorts were developed batch rotary retorts, which in turn gave place to continuous retorts – although a German batch retort has recently been described.[12] The modern industry however is almost entirely based on externally fired retorts which may be rotary; or fixed, with paddle agitators; and iron or mild steel is used until the region of weak acid (below 60%) is approached. Some account of the earlier state of the industry is given in Kausch's work[14] and descriptions have been given of the manufacture in Germany,[12,15] in the United States of America,[6,11,16] in Britain,[17,18] in Russia,[19] and in general.[20] A large German plant with an annual capacity of 6000 tons was erected at Stulln, in Bavaria, to supply hydrofluoric acid for the wartime fluorine cell installation at Falkenhagen (see page 37). This had fixed retorts fired with producer gas, 18 ft. long, 7 ft. diameter, with a central shaft carrying paddles which conveyed the reaction materials. The exit gases passed through dust removal chambers and spray catchers to water cooled tubular condensers and then to refrigerated condensers. The residual gases were water-washed in towers lined with carbon brick or with polyvinyl chloride, to give a weak acid, and finally scrubbed with caustic soda. The crude acid from the condensers was purified by fractional distillation to give a product containing 99·99% hydrogen fluoride, whilst the residual calcium sulphate was to be used as a building material, similar to plaster of Paris, although in another German plant the residue was slurried with water and pumped into the Rhine.

In some American plants, a crude acid with only 80% hydrogen fluoride has first been made[6] and one British plant also follows this practice.[17] In one of the newest American plants, however, in Kentucky, this practice is no longer followed.[11] A fluorspar with 98·5% calcium fluoride, made from crude ore having only 40 – 60% CaF_2, is mixed with 99% sulphuric acid and then passes through externally gas fired (or oil fired) rotary kilns made of $\frac{3}{4}$ in. mild steel plate and fitted with replaceable steel liners. A kiln of 6 ft.

internal diameter and 40 ft. long, rotating once per minute, has an output of 6 tons of 80% acid per day. The gases, containing 70 – 75% hydrogen fluoride, are taken off at 120°–180°C. and pass through a dust catcher and coke-packed towers to remove sulphuric acid. Then the gases may be washed in counter-current with aqueous acid to give the 80% acid, which is fractionally distilled to give anhydrous acid and a weak aqueous solution which is returned to the absorption system. In the newer plant, after removing an aqueous solution, containing sulphuric and hydrofluosilicic as well as hydrofluoric acid, in a surface cooler which follows the coke-packed towers, there follow two stages of cooling in tubular steel condensers, the first cooled with water, the second with refrigerated brine, which yield an acid containing 95 – 98% of hydrogen fluoride. The exit gases are water-washed to give some aqueous acid, and then washed with caustic soda before release to atmosphere. The crude acid is distilled through bubble cap columns which may be 3 ft. in diameter and 10 ft. high, the whole distillation system being made of copper. An acid containing over 99% of hydrogen fluoride is obtained as distillate, whilst the still residue will be the azeotrope, or a little stronger, with about 40% hydrogen fluoride.

PATENTS – PRODUCTION

There have been many patents dealing with developments, not only in methods of carrying out the reaction of fluorspar with sulphuric acid, but also in methods and processes of purification, covering separation from water, from hydrofluosilicic acid, and more recently from hydrocarbons and from sulphur dioxide, as well as more general purification procedures. Interest has been shown also in other possible processes of manufacture. In the earliest patent, it was proposed to cause calcium fluoride and sulphuric acid to react in thin layers under reduced pressure,[21] and then came a number of proposals for continuous operation of retorts provided with various methods of agitation,[22, 23, 24] a Russian patent for a rotary kiln;[25] and a proposal to heat the reaction vessel with steam or a superheated liquid.[26] Several proposals deal with additions to, or special treatment of, the reaction mixture to increase the ease of handling. Thus a bisulphate is suggested in place of sulphuric acid, and sulphates or carbonaceous materials are added to the mixture.[27] In another proposal for using acid sulphates, salts are added to maintain the mixture fluid and lower the reaction temperature, inorganic compounds such as potassium and sodium sulphates, acid alkali phosphates, or boric acid, being thus used.[28] To avoid caking and corrosion, some of the waste calcium sulphate is returned to the reaction mixture,[24] or, in several very similar patents,[29] the calcium fluoride and sulphuric acid are added separately to a body of reacting material. In another proposal to the same end, sulphuric acid is sprayed on to a hot mixture of fluorspar and calcium sulphate to avoid caking[30] and in yet another it is proposed to use the calcium fluoride not too finely ground, so that a sulphate coating forms on the surface of the granules and is removed by the tumbling action in the rotating retort.[31] A number of patents deal with methods of handling the gases coming from the retorts, and with methods of condensation, the earlier ones being more particularly concerned with aqueous acid. One proposes wooden wash towers in series, with separate cooling of the circulating solutions,[32] another is a general proposal that vapours generated by reaction of sulphuric acid with salts should be scrubbed with the hot acid being produced, various additions to the latter for purification purposes being suggested.[33] Later patents aim at the production of pure anhydrous acid. Thus it is proposed to operate a continuous retort at pressure above atmospheric, and to cool and condense in stages, removing first sulphuric acid, then aqueous hydrofluoric acid, and finally anhydrous hydrofluoric acid in a refrigeration stage.[34]

Another process proposes to maintain a high proportion of hydrogen fluoride in the gases from the retort, to pass them over calcium fluoride to remove sulphuric acid, then to separate an aqueous hydrofluoric acid in the first cooling stage.[35] In a recent patent, gaseous anhydrous hydrogen fluoride containing sulphur dioxide as an impurity is mixed with air or inert gas and scrubbed in a packed tower with water, to give an aqueous acid free from sulphur dioxide.[36] Yet again, the crude furnace gases are to be scrubbed with hot strong sulphuric acid to reduce their water content, and then compressed to a pressure of 20 lb./sq.in., before cooling and condensation.[37]

PATENTS – PURIFICATION.

While it is apparent that the condensation procedures referred to above have as an aim the production of a purer acid, some patents cover specific procedures for that purpose. Attention may here be drawn to a difference between hydrofluoric acid and hydrochloric acid: over the whole range of compositions, from pure water to pure hydrogen fluoride, hydrofluoric acids are liquid at atmospheric temperature and pressure, whereas there is a limit to the strength of hydrochloric acid which can be condensed under these conditions, and solutions having more of the acid constituent than the azeotropic composition will on distillation give a proportion of anhydrous acid, and the remainder as azeotrope. In the case of hydrofluoric acid, strong acids can readily be obtained from the production plant, *e.g.* it has been seen that one unit aims to produce an 80% acid, and a high proportion can be obtained in the anhydrous state on distillation. Thus the first purification patents claim the production of anhydrous hydrofluoric acid by fractional distillation of aqueous acid containing less water that the azeotropic composition.[38] It is proposed to remove the last traces of moisture by treatment with fluorine.[39] The use of hydrofluoric acid as a catalyst in the petroleum industry gives rise to a recovered acid in aqueous or organic solution and with various contaminants[40] and numerous processes have been proposed, mostly for recovering the anhydrous acid from aqueous solution, and this usually of azeotropic composition. Thus it is proposed to add ethylene glycol, when much of the water can be distilled off, followed by a 60% acid which can be redistilled to give anhydrous acid and azeotrope for reprocessing.[41] By carrying out the distillation in presence of an olefin, an alkyl fluoride is obtained which can itself be used as an alkylating agent;[42] or by using a *cyclo*-olefin, the organic fluoride formed can be decomposed subsequently by heating to 100-250°C. and hydrofluoric acid recovered.[43] By distilling in presence of a light hydrocarbon, substantially anhydrous hydrofluoric acid is recovered directly.[44] It has also been proposed to distil the azeotrope at pressures below atmospheric, thus separating it into aqueous solutions lower and higher in hydrogen fluoride which, when distilled at atmospheric pressure, give in one case hydrogen fluoride and azeotrope and in the other water and azeotrope,[45] to freeze out from the azeotrope, at -55°to -60°C., the compound HF,H_2O with 52% of hydrogen fluoride and then to distil anhydrous material from this;[46] and to add potassium fluoride to give KF,HF, when all the water can be distilled off and then, at a much higher temperature, the hydrogen fluoride.[47] Procedures for fractional distillation of hydrogen fluoride-hydrocarbon mixtures have also been claimed.[48]

The problem of silica in the fluorspar, with consequent presence of silicon tetrafluoride in the hydrofluoric acid, has received much attention and many solutions have been proposed. Thus, if the silicon content of the fluorspar is not too high (not more than about 3%) its prior treatment with aqueous hydrofluoric acid is proposed, the mixture being heated to drive off silicon tetrafluoride before the normal treatment with sulphuric acid.[49] Or after leaching with dilute aqueous acid the fluorspar is heated in air to

500 – 1000°C. to reduce the sulphide content, which is deleterious in causing contamination of the hydrofluoric acid with sulphur dioxide.[50] Or, what amounts to the same thing, the fluorspar is treated with 85 – 90% sulphuric acid giving a thick paste which is stirred and gently heated and, after the silicon tetrafluoride has been expelled, strong sulphuric acid is added and stronger heating applied.[51, 52] It may be presumed that the more recent fractional distillation techniques for obtaining the anhydrous acid from acids containing 80 to 95% hydrogen fluoride, will eliminate silicon tetrafluoride readily. The principal objection to this impurity is that it represents a waste of raw materials and therefore an added cost, and so the emphasis is on the removal of silica by physical means, such as flotation processes, before the fluorspar enters into reaction with sulphuric acid, as has been noted above. The proposals below are therefore mainly, though not entirely, concerned with the purification of aqueous acid. The fact that silicon tetrafluoride has a lower boiling point than hydrogen fluoride is the basis of a patent claiming that any desired degree of separation of silicon tetrafluoride and hydrogen fluoride can be achieved by condensing the mixed vapours at an appropriate low temperature.[53] A somewhat earlier patent covered very similar ground:[54] another must presumably be in error in stating that the first fractions to condense from the substantially anhydrous vapour contain the silicon tetrafluoride.[55] Yet another patent points out that from aqueous solutions containing less than, say, 65% of hydrogen fluoride this acid is preferentially volatilized and the hydrofluosilicic acid remains behind, so that the hydrofluoric acid can be purified by distillation.[56] Thus on distillation of an acid containing 40% hydrogen fluoride and 2·3% of silica, 80% was obtained as acid containing 0·2% of silica and 20% as a residue containing 11% of silica. The same specification points out that on distilling acids with more than 80% hydrogen fluoride the silicon tetrafluoride is preferentially volatilized, and a pure residue can be obtained in the still by boiling off the silicon tetrafluoride up a reflux column. An aqueous acid free from silica is obtained by boiling an acid of strength greater than the constant boiling mixture, until silicon tetrafluoride is no longer evolved.[57] An early patent, the chemistry of which seems a little dubious, proposes to hydrolyze the silicon tetrafluoride in the mixed vapours from an impure aqueous acid by maintaining them at 125°C. for some time, the hydrofluoric acid being then scrubbed out.[58] Various procedures involving the formation of silicofluorides have been proposed; the simplest washes the crude hydrofluoric acid vapour with water at 70 to 100°C., whereby hydrofluosilicic acid and sulphuric acid are removed;[59] alternatively the silicon tetrafluoride may be removed by passing the vapour over sodium fluoride at 200 to 500°[60] or over sodium acid fluoride at 80 to 250°.[61] In another process, acid contaminated with hydrofluosilicic acid reacts with alkali fluorides in such a manner as to obtain a readily filterable precipitate which is removed, and then pure acid is distilled off.[62]

One proposal is to add silicon tetrafluoride to convert everything to hydrofluosilicic acid, and then treat this with sodium or other metal fluoride to give pure hydrogen fluoride and the silicofluoride, which itself is subsequently decomposed by heat to reform the metal fluoride and silicon tetrafluoride.[63] In a process for fluosilicic acid or its salts, treatment with ammonia enables the silica to be separated and the resulting solution of ammonium fluoride is mixed with an equivalent amount of alkali fluoride and evaporated to dryness: it is said that ammonia then escapes leaving the equivalent amount of acid alkali fluoride which, on further heating, evolves anhydrous hydrofluoric acid leaving a residue of alkali fluoride.[64] It has been proposed to wash the crude vapours with a hot solution of potassium sulphate, so that while hydrofluoric acid is not absorbed potassium silicofluoride is precipitated.[65] If ferric oxide is

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added to the aqueous acid, the silicofluoride may be filtered off and the ferric fluoride crystallized out and decomposed with steam.[66]

A German process proposes to wash the crude gases with sulphuric acid,[67] and whilst it does not refer to the formation of fluorosulphonic acid, this is implicit in the specification; 50 parts of 100% sulphuric acid absorb an equal amount of hydrofluoric acid which is equivalent to 1 mole of the former to 5 of the latter. Silicon tetrafluoride is not absorbed at 30°C., the operating temperature. Then by heating to 60 – 80°C. four fifths of the hydrofluoric acid may be boiled out in a pure form. The residual acid may be used for treating more calcium fluoride, and obviously it retains one mole of hydrofluoric acid and consists of fluorosulphonic acid. If water is present in the crude gases going to the scrubber, an equivalent amount of sulphur trioxide is added to the sulphuric acid. A later American specification covers much the same ground, but more clearly claims fluorosulphonic acid itself as the scrubbing agent.[68] The stripping of the acid is carried out in a fractionating column and the temperature in the boiler is taken up to 160°C., substantially the boiling point of fluorosulphonic acid, so that the recovery of the hydrofluoric acid is essentially complete.

Sulphur dioxide is an impurity liable to occur in crude acid owing to reduction of the sulphuric acid *e.g.*, by sulphides in the fluorspar, or by organic matter. This impurity is disadvantageous in hydrofluoric acid used as catalyst in the petroleum industry, and a number of proposals have been made for its removal. Thus the crude acid, containing 0·1 to 1·0% of sulphur dioxide, may be treated with olefinic compounds to give sulphur-containing organic compounds insoluble in the aqueous acid.[69] It is suggested that a hydrocarbon, between propane and pentane, if added to the crude anhydrous acid, will form a minimum boiling azeotrope with sulphur dioxide, which may be separated by distillation, giving a purified product with only 1 p.p.m. of sulphur dioxide.[70] If the crude acid is treated with spent hydrofluoric acid from the alkylation process, olefinic oils present in the latter will react to form complex compounds with the sulphur dioxide so that pure hydrofluoric acid can be distilled off.[71] A simple proposal is to reduce the sulphur dioxide with hydrogen sulphide and distil off a pure acid,[72] which will, however, contain more water as a result of the reaction.

PATENTS - OTHER PROCESSES

There have been proposals to make hydrofluoric acid by processes other than the treatment of fluorspar with sulphuric acid. A Norwegian patent describes the reaction of fluorspar with silica at an elevated temperature and in presence of water vapour.[73] By varying the proportion of water vapour it is possible to obtain either hydrofluosilicic acid, according to the equation:-

$$3CaF_2 + SiO_2 + H_2O \rightarrow H_2SiF_6 + 3CaO$$

or hydrofluoric acid itself:-

$$3CaF_2 + SiO_2 + 3H_2O \rightarrow 6HF + CaSiO_3 + 2CaO.$$

It is not obvious why excess silica should not be added to convert all the lime to calcium silicate, as this would be expected to favour the hydrolysis of fluorspar, which, from Domange's results (see page 73), gives rise to only 2·3% of hydrogen fluoride in the equilibrium mixture with water vapour at 1100°C. A Belgian patent proposes fusing together in an electric furnace hydrous raw material containing fluorine with silica and alumina, and recovering hydrofluoric acid from the gases evolved.[74] According to a Russian patent, fluorspar is heated with the oxides or hydroxides of iron or aluminium in an atmosphere of water vapour to give hydrofluoric acid.[75] It is not obvious that any such processes will be advantageous compared with the fluorspar-sulphuric acid process as now developed.

An interesting proposal in another patent is a combined production and recovery process.[76] Hydrofluoric acid, for example that recovered from catalysis in the petroleum industry, reacts in the presence of air or oxygen with a metal such as silver, copper, lead or mercury to give the metal fluoride; this is then reduced by hydrogen, or by hydrocarbons, to give pure hydrofluoric acid. Among other recovery processes, one worth noting describes the recovery of hydrofluoric acid from the gases from phosphoric acid plants, by washing them with hot aqueous solutions so that no condensation of water vapour occurs,[77] and a number of patents, all covering distillation procedures, deal with the recovery of hydrofluoric acid from admixtures with hydrochloric acid and organic materials, arising in the production of such compounds as fluorochloromethanes.[78] And one patent deals with the purification of hydrofluoric acid made in the production of fluorocarbons by means of extraction with a fluorocarbon.[79]

HYDROFLUORIC ACID FROM FRÉMY'S SALT.

The classical method of preparing anhydrous hydrofluoric acid is by decomposing Frémy's salt, KHF_2, obtained by half neutralizing aqueous hydrofluoric acid with potash and evaporating the solution to crystallization. This is a derived process, in that hydrofluoric acid must first be made, presumably from fluorspar. Whilst the aqueous process is usual for this salt, it has been claimed in a patent that the treatment of solid potassium chloride with hydrofluoric acid vapour can be used to made Frémy's salt,[80] and that working at temperatures not above 50°C. with an excess of hydrofluoric acid, liquid polyfluorides may be obtained. Elsewhere it is said that potassium sulphide may be used in place of potassium chloride.[81]

It has already been seen that the preparation of hydrofluoric acid sufficiently low in moisture was one of the principal problems in the satisfactory operation of high temperature fluorine cells (see page 29), and this in turn depended on the adequate dehydration of the potassium bifluoride. Simons has described the preparation on several occasions.[82] Dehydration is effected by electrolyzing the molten salt at 200 – 220°, using a graphite anode in a copper pot, until fluorine is evolved, when the dehydration is complete; and anhydrous acid is obtained on further heating, using a ring burner to heat the melt near the surface, to avoid frothing.

In his extensive work on the properties of anhydrous hydrofluoric acid as a solvent, Fredenhagen required considerable quantities, and as these were made by the method under discussion, it has been described in some detail,[83] and has been further studied by Fredenhagen and Cadenbach.[84] The salt melts, not very sharply, between 215° and 225°C., and at about 400° the pressure of hydrofluoric acid vapour reaches 1 atm. The loss of acid causes a rise in temperature, as the potassium fluoride produced dissolves in the melt. When 30% of the hydrofluoric acid has been evolved, the melt is saturated with potassium fluoride (it then contains 17·9% HF, compared with 25·6% in the original salt) and the evolution of hydrofluoric acid continues at atmospheric pressure at a constant temperature of 504°C., the further potassium fluoride formed appearing as a solid phase. These observations are considered to explain the foaming phenomena referred to by previous authors. In the first stage, a large proportion of the heat applied is used in heating up the melt; but when a steady temperature is reached a greater proportion of the heat is available for decomposing the salt so that the rate of hydrofluoric acid evolution is much increased and foaming may occur, this being assisted by the presence of a solid phase. If water is present in the original salt the temperature at which the hydrofluoric acid pressure reaches 1 atmosphere is higher, to the extent, *e.g.*, of about 5° with a salt containing 2% of water. The water is quite strongly held, and comes off only slowly with the hydrofluoric acid, the temperature of the decomposing melt falling gradually to the m.p. of the anhydrous salt.

The water content of the acid and the preparation of acid of low water content are dealt with below, (see page 87). It is shown that the electrical conductivity is a guide to the water content and that to collect material really low in water content, about the first 30% of acid distilling over should be rejected and the remainder should be redistilled from well calcined potassium fluoride.

In a patent resulting from this work[83] it was proposed that the potassium bifluoride should be dried by heating in a stream of dry air, keeping the temperature below the melting point, until the hydrofluoric acid evolved on heating a small portion to its decomposition temperature has a specific conductivity below a specified limit (0·02 mho/0°C.) More nearly anhydrous acid could be obtained on redistilling the first product.[84] Special care should be taken, in the heating, to prevent trouble from too rapid gas evolution[86] by reducing the rate of heating when the maximum temperature of the melt is reached. The thermodynamics of the system $KHF_2 - KF - HF$ have been studied;[87] over the temperature range 205 – 303°C., the dissociation pressure of β-KHF_2 is given by $\log P_{mm} = -\frac{4000}{T} + 8{\cdot}574$; at 303°, $P = 44{\cdot}4$ mm., and extrapolating this expression gives $P = 760$ mm. at 429°C., which is in very fair agreement with the experimental observation of Fredenhagen and Cadenbach.

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SECTION IV.

THE PHYSICAL AND CHEMICAL PROPERTIES AND USES OF HYDROGEN FLUORIDE AND ITS AQUEOUS SOLUTIONS.

By H. R. LEECH

THE PHYSICAL PROPERTIES OF HYDROFLUORIC ACID.

THE PHYSICAL PROPERTIES OF THE PURE SUBSTANCE

The melting point of hydrofluoric acid has been given as 190·09°K., (-83·04°C.)[1] and 190°K.[2] The density of the solid has been given as[3]

t, °C.	−97·2	−93·8	−191
d, g./c.c.	1·658	1·653	1·749

From these figures the coefficient of expansion of the solid is given as 60×10^{-5}. It is pointed out in this work that when quite free from moisture, liquid hydrofluoric acid does not attack fused quartz, which was therefore used. This confirms an observation by Fredenhagen (see page 137). Between −75° and +5°C. the density of the liquid has been expressed by the equation[4] (t = temperature, °C.)

$$d_t = 1{\cdot}0020 - 2{\cdot}2625\times10^{-3}t + 3{\cdot}125\times10^{-6}t^2 \quad (\text{g./c.c.})$$

from which the following values can be calculated

t, °C.	−80	−60	−40	−20	0	+20
d, g./c.c.	1·2030	1·1490	1·0975	1·0483	1·0020	0·9580

The vapour pressure of hydrogen fluoride between 5 and 76 cm./Hg is given by[5] $\log_{10}P(\text{cm}) = 6{\cdot}3739 - \dfrac{1316{\cdot}79}{T}$ An earlier determination was in good agreement with this giving over a wider range – from the melting point to 47°C. – the equation[2] $\log_{10}P(\text{cm}) = 6{\cdot}37 - \dfrac{1315}{T}$. Over a narrow range (15 to 24°C.) a different equation has been proposed:[6]

$$\log P(\text{cm}) = 7{\cdot}48 - \frac{1345{\cdot}3}{T}.$$

The corresponding boiling points at 760 mm. are[2,5,6] 19·6°, 19·94° and 19·54°. The vapour pressure of deuterium fluoride is given by

$$\log_{10}P(\text{cm}) = 6{\cdot}2026 - \frac{1261{\cdot}16}{T},$$

and the atmospheric boiling point is 18·68°C.[5] The comparative values of the vapour pressures of hydrogen fluoride (P_1) and deuterium fluoride (P_2), in cm. of mercury, are given in Table I.

The plot of $\log \dfrac{P_1}{P_2}$ v. $\dfrac{1}{T}$ slopes the same way for this pair and for the acetic acid pair, where association also occurs, and in the opposite sense for the corresponding hydrogen-deuterium pairs in the case of water, ammonia, and hydrogen chloride. It is suggested that hydrofluoric acid might lend itself to economic distillation at low pressures for separating hydrogen isotopes: the deuterium fluoride would be removed at the top of the still,

TABLE I. - VAPOUR PRESSURES OF HYDROGEN FLUORIDE AND DEUTERIUM FLUORIDE

T °K	240	250	260	270	280	290
P_1	7·71	12·78	20·38	31·40	46·89	68·11
P_2	8·87	14·39	22·49	34·01	49·95	71·42
P_2/P_1	1·150	1·126	1·104	1·083	1·065	1·049

which would be very advantageous. The hydrogen and deuterium fluorides used in this work were made by reduction of silver fluoride. The critical temperature for hydrogen fluoride is 230·2°C.,[7] and the value of van Laar's constant, $K = T_c/T_b$ derived from this, 1·72, is close to the values for the other hydrogen halides. From a comparison of the critical data of related compounds, the critical density was estimated to be 0·416 g./c.c.[8] The vapour density is considered below in relation to the association of hydrofluoric acid. The specific heat of the solid, from 11° to 77°K., is given in Table II.[9]

TABLE II. - MOLAR HEAT CAPACITY OF SOLID HYDROFLUORIC ACID, 11-77°K.

T, °K.	11.02	13.34	13.36	15.50	16.26	18.75	19.32	21.20	23.0	26.6
C_p g.-cal.	0.11	0.19	0.20	0.31	0.38	0.50	0.54	0.71	0.87	1.18
T. °K.	29.7	33.7	38.1	42.7	48.7	54.6	60.9	65.8	71.3	77.4
C_p g.-cal.	1.46	1.82	2.14	2.50	2.85	3.22	3.52	3.81	3.95	4.20

The molar heat capacity is given for a molecular weight of 20, but this is very arbitrary, since there is every indication of association and a much higher molecular weight (see below).

The specific heats have been determined also from 98° to the melting point (Table III). In this work rather a wide scatter was shown in the results, so the following values were obtained by graphic interpolation[1].

TABLE III. - SPECIFIC HEAT OF SOLID HYDROFLUORIC ACID, 100°K.- m.p.

T, °K.	100	110	120	130	140	150	160	170	180
C_p g.-cal.	5.95	6.63	7.05	7.45	7.88	8.35	8.70	9.72	10.75

The results did not lie on one smooth curve, there was some suggestion of transformations occurring at 118° and 167°K., and there was, of course, a pronounced discontinuity at the melting point. The curves for these results and for those of Clusius *et al.* above for the lower temperature range, also did not seem to be congruent, so that it appeared as if there was another transformation between 80 and 90°K. The average value of the latent heat of fusion determined in this work was 1094 g.-cal. per 20 g., with a mean error of ± 13 g.-cal. The authors point out that the value of the ratio of this 'molar latent heat' to the melting point on the absolute scale, is 5·7 which is indicative of association; the ratio for water is 5·3 whilst that for the other hydrogen halides is 3·4.

The specific heat of the liquid, determined by the same workers[1], is given in Table IV; again the results showed scatter and the following values were taken from the smoothed curve.

TABLE IV. - SPECIFIC HEAT OF LIQUID HYDROFLUORIC ACID, m.p. – 270°K.

T °K.	200	210	220	230	240	250	260	270
Cp, g.-cal.	13·45	13·72	14·12	14·60	15·10	15·65	16·20	16·75

The latent heat of vaporization has been considered from the point of view of the effect of molecular association. Simons determined the vapour pressure curve, and by applying the Clapeyron-Clausius equation obtained a figure of 6125 g.-cal. per g. mole which, it was pointed out, was only approximate,[2] since hydrofluoric acid, in the region considered, was far from obeying the gas laws.

It was remarked that this figure, like previously reported figures of the same order, *e.g.* figures derived from Trouton's rule, applies to a molecule of formula H_3F_3, and for a simple molecule of HF of molecular weight 20 a figure of 1927 ± 90 g.-cal. was calculated for the latent heat using Simons' data.[10] Returning to the question some time later,[11] Simons made an experimental determination of the latent heat at 750 mm. pressure, and obtained a value of 97·5 g.-cal./g., whilst, taking a corrected figure of 6025 g.-cal. for the 'molar' latent heat and dividing this by the molecular weight obtained from vapour density determinations, a value of 95 g.-cal./g. was obtained. Fredenhagen and co-workers obtained somewhat different figures.[6] They actually determined values of 85·23 and 87·55 g.-cal./g. at 4·40° and 15·76°C. respectively, and from careful measurement of vapour pressures over the range 650 – 900 mm. (15 – 24°C.) they obtained a value of 6150 g.-cal. per g. mole. They had obtained, from vapour density data, an association factor of 3·45, so that the latent heat is 89·1 g.-cal./g. (± 1·25).

The heat capacity of gaseous hydrofluoric acid in the monomeric form, i.e. HF, assuming no association, has been calculated from spectroscopic data.[12] The values, together with the free energy and entropy calculated by the same authors, are given in Table V.

TABLE V. - THERMODYNAMIC PROPERTIES OF HYDROFLUORIC ACID

T, °K.	$-(F^\circ - H_0^\circ)/T$	S°	Cp°
298·1	34·634	41·527	6·963
300	34·677	41·571	6·963
400	36·663	43·574	6·966
500	38·207	45·130	6·969
600	39·470	46·401	6·986
800	41·467	48·420	7·065
1000	43·023	50·012	7·214
1200	44·301	51·343	7·408
1400	45·392	52·501	7·612
1600	46·346	53·531	7·812
1800	47·197	54·461	7·992
2000	47·968	55·314	8·152

The electrical conductivity of liquid hydrogen fluoride is very greatly increased by traces of water and other impurities. The best, i.e. the lowest, value obtained by Fredenhagen and Cadenbach was 14 × 10^{-6} ohm^{-1} at –15°C., but it was thought that this was not the lowest value possible.[13] The material for this work was made by heating Frémy's salt; when the salt used contained 2% of moisture very high conductivities were shown in the acid first made, whilst salt previously well dried gave a product which showed much lower initial conductivities. The effect of some salt spray on the conductivity must also be taken into account. Successive fractions were collected and showed rapidly decreasing values of the conductivity. When the material of better quality was collected and successive fractions were distilled into the conductivity apparatus, even lower values were obtained, because of the strong retention of small amounts of water in the liquid phase on distillation. The earlier successive samples show a decrease in conductivity because adsorbed water is washed out by the first fractions, but later samples show a progressive increase because the accumulation of water in the liquid phase leads to some distilling over. Results are shown in Table VI: the first fraction from the undried salt had a water content above 2N., that from the dried salt only about 0·05N.

TABLE VI.- PRODUCTION OF LOW MOISTURE-CONTENT HYDROFLUORIC ACID

Specific conductivity × 10^6, at -15°C.			
*A*1	*A*2	*B*3	*B*4
260,000	6,700	87	135
74,400	3,600	50	48
16,100	3,500	32	26
5,800	2,400	30	23
3,100	1,800	35	19
5,000	1,100	46	14
2,850	510	52	17
2,120	630	65	21
980	640	69	25
680		98	29
			36
			119

A. – successive samples on heating KHF_2

*A*1 – salt with 2% moisture.
*A*2 – well dried salt.

B. – First 30% of product on heating KHF_2 discarded, further products condensed as successive samples on distillation: two series of experiments, 3 and 4.

In an earlier paper[14] some values of the conductivity for increasing water content were given, but these must be somewhat in error, as at that time the lowest conductivity achieved was 40×10^{-6}. (See page 87).

The dielectric constant is given in Table VII[15] for acid of lowest possible water content.

TABLE VII.- DIELECTRIC CONSTANT OF LIQUID HYDROFLUORIC ACID

t, °C.	-73	-70	-42	-27	0
ϵ	174·8	173·2	134·2	110·6	83·6

The ionization potential was estimated, or predicted, to be 15·7 ± 0·7 V.[16] 14·02 V.[17] and 18·04 V.[18] More recent actual determinations quote a figure of 5·4 e.V., but no explanation is offered of the discrepancy.[19] Some observations have been made on the nuclear magnetic resonance of liquid hydrofluoric acid.[20]

The viscosity of the pure liquid has been determined over a range of temperatures, and compared with the commercial acid as obtained from a cylinder (though no analysis is given) and with acid to which ethyl alcohol had been added to give 6·1 mol.-% alcohol and 0·5 mol.-% water.[21] The results are given in Table VIII in centistokes, with the values for the pure compound in centipoises also, calculated using the known density values.

The viscosity is low, comparable with that of ethyl ether, and it is seen to be very remarkably increased by relatively small amounts of impurities.

TABLE VIII. - VISCOSITY OF PURE AND CONTAMINATED HYDROFLUORIC ACIDS

Temperature °C.	Viscosity, centistokes			Centipoises pure acid
	Comm'l. Acid	Acid and Alcohol	Pure Acid	
-68·75	0·893	—	0·780	0·914
62·5	0·797	0·983	0·668	0·772
56·25	0·720	0·878	0·585	0·666
50·0	0·645	0·788	0·507	0·570
43·75	0·579	0·720	0·450	0·498
37·5	0·525	0·668	0·397	0·434
31·25	0·472	0·615	0·360	0·387
25·0	0·420	0·575	0·330	0·350
18·75	0·377	0·533	0·306	0·320
12·5	0·353	0·499	0·285	0·296
6·25	0·330	0·470	0·270	0·274
0	0·310	0·447	0·256	0·256
+6·25	—	—	0·243	0·240

The surface tension of liquid hydrofluoric acid is[4]

t °C.	-81·8	-23·2	+18·2
γ	17·7	12·0	8·62 dynes/cm.

The results fit the equation $\gamma = 40{\cdot}7\,[1 - \frac{T}{503{\cdot}2}]^{1{\cdot}78}$

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THE HYDROGEN FLUORIDE MOLECULE

The vapour density of hydrogen fluoride is much greater than would be expected for the simple molecule HF, indicating considerable association. The earliest explanation was the suggestion of a dimeric form H_2F_2, but the density shows that the association must be greater than this; a later suggestion was that a hexamer, $(HF)_6$, was formed, and that the equilibrium $6HF \rightleftharpoons (HF)_6$ existed. Hydrogen bonding, which is stronger in this than in any other case, is the cause of the association, which it now appears leads to the formation of zig-zag chains containing up to eight HF units. The evidence for this is well authenticated in the vapour at moderate temperatures, and the solid also has been shown to be constructed of similar, endless chains.

A number of determinations of the vapour density have been reported. Simons and Hildebrand, 1924,[1] bubbled dry nitrogen through liquid anhydrous hydrofluoric acid, and absorbed the vapour in solid sodium fluoride. The vapour density was calculated from the data obtained, using the vapour pressure determined by the same authors (Table IX).

TABLE IX.- VAPOUR DENSITY (H=2) OF SATURATED HF
(SIMONS AND HILDEBRAND)

temp. °C.	-39	-21	-10	0	+5·2	+8·5	+12	+16
p, mm.	56·2	144	234	364	436	491	576	661
vap. density	87·4	81·6	74·3	67·6	69·3	64·3	69·5	47·7

Fredenhagen (1933)[2] also saturated a carrier gas with the vapour, which was absorbed in potash, to determine the density of saturated vapour between the freezing point and +4°C. (Table X).

TABLE X.- VAPOUR DENSITY (H=2) OF SATURATED HF
(FREDENHAGEN)

temp. °C.	-78·0	-55·0	-45·0	-34·6	-21·7	-12·44	0	+4·44
p, mm.	4·23	22·0	40·04	71·46	136·8	210	364	425·7
vap. density	74·19	79·84	82·34	85·47	83·42	77·31	73·72	70·21

The results were, except in one case, in good agreement with those of Simons and Hildebrand. The vapour density shows a maximum at -34°; attributed to the fact that whilst the degree of association increases as the temperature falls, it diminishes with falling pressure, and the pressure effect outweighs the temperature effect below -34°C.

The carrier gas method was considered unreliable above 4°C. owing to the high partial pressure of the hydrogen fluoride, so a further series of determinations was made of the density of unsaturated vapour at higher temperatures, by measuring the weight of gas in a silver bulb at atmospheric pressure. Excess of liquid was put in the bulb, which was then brought to equilibrium (excess liquid boiled off) and the residual vapour estimated by absorbing it in water and titrating the acid. The results in Table XI are compared with the classical determinations of Thorpe and Hambley. There is good agreement above 45°C. but below this temperature the later values are somewhat higher, perhaps because Thorpe and Hambley did not displace the air completely from their bulbs.

Fredenhagen, Klatt and Kunz (1934)[3] made a more extended series of determinations, at 26°, 32°, and 38°C., to give the 'dissociation isotherms' which are shown in Fig. 1.

Long, Hildebrand and Morrell (1943)[4] in order specifically to study the the association, observed the variation of pressure with temperature for a given initial volume of hydrogen fluoride, and in their experimental work

TABLE XI. - VAPOUR DENSITY (H=2) OF HF AT ATMOSPHERIC PRESSURE, 24°–80° C.

t, °C.	*d*(F)	*d*(T&H)	*t*, °C.	*d*(F)	*d*(T&H)	*t*, °C.	*d*(F)	*d*(T&H)
23·58	62·8		33·1		38·12	42·8		26·26
24·02	61·45		33·8		36·66	45·6	24·91	
25·30	57·90		35·0	35·67		47·3		23·76
25·90	57·78		36·3		32·20	49·8	22·61	
26·4		51·18	36·55	32·83		55·1	21·71	
27·4	52·59		37·90	31·44		57·5		21·28
27·8		49·42	38·7		29·46	59·90	21·31	
29·2		45·54	38·85	29·80		69·4		20·96
29·8	46·02		39·2		28·94	70·20	21·00	
32·0		39·74	40·4	28·35		79·30	20·58	
32·8	39·53		41·20	27·99		88·1		20·58

several features are of interest. Discrepancies in their early experiments were traced to the presence of a small amount of moisture and they concluded that water and hydrofluoric acid evidently form a gaseous hydrate more stable than the hydrofluoric acid polymer, each water molecule being probably surrounded by several hydrofluoric acid molecules. The association factor will therefore be much higher if any water is present, which may explain disparities in results published by other workers. They made their hydrofluoric acid by reducing silver fluoride with hydrogen, whereas previous workers generally made it by decomposing Frémy's salt. They had previously used the same method for hydrogen and deuterium fluorides, as has been noted above. They measured pressures using a null-point gauge, made

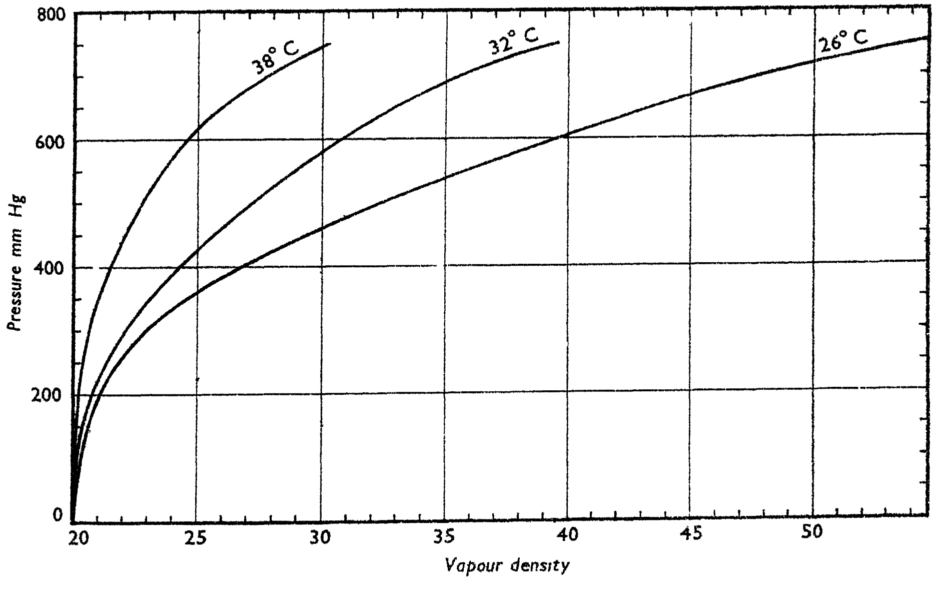
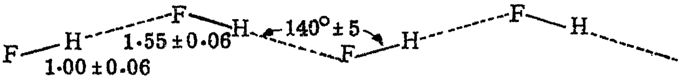


Fig. 1. 'DISSOCIATION ISOTHERMS' FOR HYDROGEN FLUORIDE

of a fine gold casing with a corrugated gold-plated brass diaphragm. As these workers give no actual densities, but only association factors, their results are considered below.

Since the molecular weight of the simple HF molecule is 20, the extent of the association is obvious from the above figures. Association decreases rapidly as temperature increases, so that above 80°C. it is practically nil. It also decreases rapidly as the pressure falls, becoming negligibly small at about 50 mm. at 26°, at 100 mm., at 32°, and at 150 mm. at 38°. Simons and Hildebrand studied their results from the standpoint of polymerization to the hexamer (it was obvious that, with apparent molecular weights above 80, molecules higher than the tetramer must be formed). Both these results and those of Thorpe and Hambley fitted an equilibrium of the form $6HF \rightleftharpoons (HF)_6$, and the heat of association appeared to be 40,000 g.-cal. per g.-molecule of hexamer. Whilst subsequent work has cast doubt on the simplicity of this assumption, which also suggested a ring form for the polymer molecule, Hildebrand recurred to it in a later paper.[4] Though Fredenhagen doubted the validity of the hexamer hypothesis, he was at pains to demonstrate the association from several angles. Thus he determined the latent heat of evaporation calorimetrically as 1704·6 g.-cal./20 g. at 4·4°, 1751 g.-cal./20 g at 15·76°, whilst the vapour pressure data gave a mean molecular latent heat at 19·54° of 6150 g.-cal. The association factor must therefore be $\frac{6150}{1751}=3{\cdot}51$ and the molecular weight 70·2, which though high is in fair agreement with the results given above. Similarly the vapour pressure lowering, by solutes dissolved in liquid hydrofluoric acid, was shown to be greater by a factor of 3·5 than that calculated from a molecular weight of 20 for the solvent. It was therefore concluded that the degree of association in the liquid phase was of the same order as in the vapour. A further paper[5] described measurements of the latent heat when liquid hydrofluoric acid was evaporated at its atmospheric boiling point and expanded through a valve to 20 mm. pressure (when it would be almost completely monomeric). A value of 7,800 g.-cal. per 20 g. of hydrogen fluoride was obtained, and as a figure of 1780 g.-cal./20 g. had already been obtained for the latent heat at this temperature and atmospheric pressure, the difference, 6020 g.-cal., must be the dissociation energy. For the average association factor of 3·5, the association energy is therefore 21,070 g.-cal., and for $(HF)_6$, the value is 36,120 g.-cal., in very fair agreement with the figure of 40,000 g.-cal. deduced by Simons and Hildebrand. In a re-examination of these data, and a comparison of the behaviour of hydrogen fluoride and deuterium fluoride, Hildebrand[4] obtained figures of 40,800 and 41,100 g.-cal. for the respective heats of association to an assumed hexameric form.

Simons returned to the question with a study of the electron diffraction of the vapour.[6] The results could not be interpreted in terms of molecules with a hexagonal structure, but could readily be explained in terms of a zig-zag chain, and also seemed to show that polymers of different chain lengths were present. The nature of these chains, and the dimensions (in Ångstroms) are given in the diagram:



The hydrogen atoms are in line with the fluorine atoms within ± 15°. Evidence was also brought forward suggesting that the anomalous values of certain properties of the liquid would be explicable on the basis of chain polymer formation.

Refs. p. 100

At this time the X-ray structure of the solid was reported.[7] The crystals are tetragonal or pseudo-tetragonal; at 91°K. a_0 = 5·45; c_0 = 9·95A. There are infinite zig-zag chains along the c-axis; four chains each of four hydrogen fluoride molecules make the unit cell. The distance F-H-F is 2·7A., compared with 2·55 in the electron diffraction studies above, the chain angle being 134°, compared with 140°: the good agreement with the electron diffraction results on the vapour was remarked, although in a later note a tribute was also paid to Fredenhagen.[8]

Long, Hildebrand and Morell[4] expressed their results in terms of the association factor. The gas law can be expressed in the form $\frac{P}{T} = \frac{nR}{V}$. For a given quantity of gas, if at a temperature T_1, and corresponding value n_1 for the number of moles of gas, the gas is completely unassociated, the association factor for any other condition is $\frac{n_1}{n}$ Allowing for the expansion of the containing vessel (expansion coefficient = α), $\frac{n_1}{n} = z = \frac{P_1/T_1}{P/T} \times \frac{(1+\alpha t_1)}{(1+\alpha t)}$. The data in Table XII were given by these workers, as obtained by graphical interpolation from the actual experimental results. They show the variation of z with P at a series of temperatures, and also the value of $-\log K$, where K is the equilibrium constant for the reaction $6HF \rightleftharpoons (HF)_6$ (It is shown that $K = \frac{5^5(z-1)}{P^5(6-z)^6}$).

TABLE XII. - ISOTHERMS FOR HF AND $-\log K$ FOR EQUILIBRIUM $6HF \rightleftharpoons (HF)_6$.

T, °K.	P mm.	z	$-\log K$	T, °K.	P mm.	z	$-\log K$
273·15	244·5	3·118	10·78	305	561·5	1·510	14·45
	230·2	2·953	10·93		528	1·434	14·44
	216·9	2·750	11·02		492·5	1·347	14·43
	209·7	2·673	11·00		477	1·315	14·42
	200·2	2·597	11·00		476	1·322	14·41
286	348	2·297	12·51		462	1·285	14·42
	328·5	2·162	12·53		457	1·295	14·37
	311	2·013	12·57		453	1·283	14·38
	300	1·955	12·55		451	1·285	14·36
	287·5	1·890	12·53		402	1·210	14·29
299	488·5	1·708	13·90		378·5	1·179	14·24
	460·5	1·614	13·89	311	639	1·354	14·99
	433	1·508	13·90		596	1·294	14·95
	418	1·464	13·89		551	1·231	14·92
	418	1·475	13·87		528·5	1·207	14·89
	407	1·415	13·90		528·5	1·215	14·87
	404	1·437	13·85		511	1·184	14·88
	401	1·422	13·86		506	1·193	14·83
	399	1·417	13·86		501	1·184	14·84
	360	1·323	13·80		498	1·185	14·72
	342·5	1·279	13·78		436	1·138	14·68
					407	1·118	14·61

Good agreement is found with Fredenhagen at 305°K. (32°C.); but the results are rather higher than his at 299° and 311°K., and reasons are suggested for casting some doubt on Fredenhagen's results. From consideration of the log K values, it is concluded that at the lower temperatures the results could be explained by the presence of higher polymers; at higher temperatures lower polymers appear to be present. Thus although the results are remarkably well covered by the simple hexameric association, it would appear that this is an over-simplification, and the formation of a series of chain polymers is a more satisfactory explanation. In a later paper[9] this position is pretty well accepted. The plot of log K against $\frac{1}{T}$ shows a slight curvature: neglecting this, the equation is $\log K = \frac{8910}{T} - 43{\cdot}65$, which agrees well with Simons and Hildebrand's equation over a smaller range, and gives, for the formation of one mole of hexamer, $H = -40{,}800$ g.-cal.

The association of hydrogen fluoride was considered from the general point of view of hydrogen bonding by Pauling.[10] He was able to show reasons for the formation of very strong hydrogen bonds by fluorine, on the basis of his electronegativity scale, and this is evidenced not only by the association of hydrogen fluoride, but also by the formation of the HF_2^- ion. The ring form of the hexameric polymer would be expected to be somewhat more stable than other polymers.

The polymerization of hydrogen fluoride as a 'chain association' was studied in a number of papers by Briegleb. He pointed out that this is the first example of a chain association in the gas phase, using subsidiary valence forces. The behaviour of hydrogen fluoride in this respect is like that of alcohol and phenol in neutral solvents, but in the vapour phase disturbing solvation effects do not arise.[11] From Fredenhagen's data on vapour densities, it is possible to calculate the proportion of the different molecular species at each temperature and pressure, and, therefore, the different equilibrium constants. Fig. 2, from Briegleb, shows the distribution of molecular species, as the percentage of the total molecules present having a given association number. It appears, for example, that at 28° and 700 mm. the distribution is roughly as follows:

Molecule	HF	$(HF)_2$	$(HF)_3$	$(HF)_4$	$(HF)_5$	$(HF)_6$	$(HF)_7$	$(HF)_8$
% of total	70	3	5.2	5.3	4.5	4.2	2.9	2.0

In a later paper[12] it was pointed out that 28° had been taken in error instead of 26°, in Fredenhagen's results, and the above data are probably slightly in error; some corrections were given of other figures in the original paper. In the generalised polymerization reaction,

$$(HF)_n + (HF)_1 \rightleftharpoons (HF)_{n+1}$$

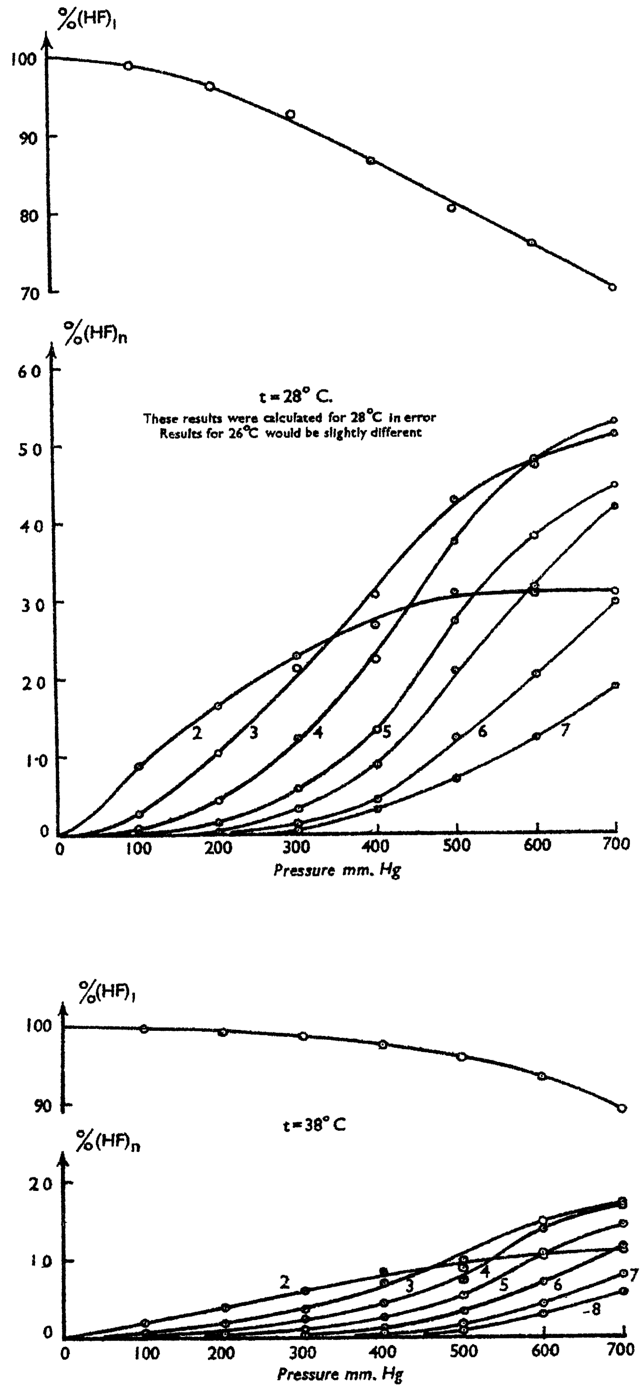
the equilibrium constant is $k_{n(n+1)} = \frac{p_{n+1}}{p_n p_1} = \frac{k_{1(n+1)}}{k_{1n}}$

The data of table XIII were given:-

TABLE XIII. - EQUILIBRIUM CONSTANTS AND THERMOCHEMISTRY OF HF POLYMERIZATION

$k_{n(n+1)}$	$T = 299°$K	$T = 311°$K.	$W_{n(n+1)}$ kg.- cal.
$K_{12} \times 10^3$	0·09	0·02	23,130 ± 3 - 4
$K_{23} \times 10^3$	3·33	2·50	4,409 ± 50%
$K_{34} \times 10^3$	2·10	1·60	4,182 ± 50%
$K_{45} \times 10^3$	1·75	1·31	4,489 ± 50%
$K_{56} \times 10^3$	1·91	1·29	6,036 ± 50%
$K_{67} \times 10^3$	1·38	1·11	4,403 ± 50%
$K_{78} \times 10^3$	1·31	1·13	4,105 ± 50%

It appears, from the reaction heats, that the formation of the first polymer, the dimer, involves a much stronger bond than any later polymers (although doubt was subsequently cast on this). The further lengthening of the chain by addition of another hydrogen fluoride molecule seems to have about the same thermal effect independent of the chain length.

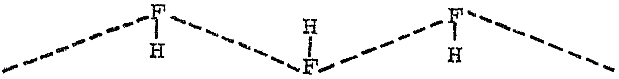


t = 28° C.
These results were calculated for 28°C in error
Results for 26°C would be slightly different

t = 38° C

Fig. 2. DISTRIBUTION OF MOLECULAR SPECIES $(HF)_{n(=1-8)}$ IN HF VAPOUR AT 28° AND 38°C. – INFLUENCE OF PRESSURE.

Briegleb, considering the theoretical interpretation of these results, concluded that neither quantum-mechanical resonance nor dipole attraction would suffice to account for the hydrogen bonding in the polymers.[11] A model was proposed in which the polymer chains are composed of hydrogen ions and fluoride ions, and by considering the Coulomb interactions and the polarization effects, it was possible to explain the experimental data. Computed results in accordance with the electron diffraction dimensions were obtained, and binding energies of the same order as those calculated above. The polymer chains were different from those suggested by the electron diffraction data, however, in that the hydrogen atoms were not in line with the F - F atoms, but in the troughs of the chain:



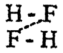
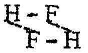
the chain angle being 135° A generalized treatment of a system showing association of the character now under consideration was attempted by Kreuzer, and a series of equations developed inter-relating functions of the concentration of each molecular species and the heat of association.[13] Fredenhagen's data were re-examined in the light of these equations, and some doubt was cast on the accuracy of the data at lower pressures. It was concluded that the mean heat of association was 10 ± 3 kg.-cal. for each associated bond. Briegleb then re-examined his results[14] and considered that in view of the doubt regarding the low pressure data, his high value for the heat of association in the formation of the dimer was not proven. It could not be shown whether the heat of association was diminishing as the chain molecule increased in length; all that could be said was that the mean value, of 10 kg.-cal., was about twice the association energy in $(R.OH)_n$ supermolecules. Briegleb has also given other accounts of this work.[15] It has been seen that values had been obtained earlier for the heat of association: thus Fredenhagen determined 6·02 kg.-cal. per 20 g. of hydrogen fluoride or 21·0 kg.-cal. for the average association factor 3·5. But this involves only 2·5 bonds, so that this gives a figure of 8·4 kg.-cal. per bond. The results of Simons and Hildebrand give similar figures.

The model proposed by Briegleb is based essentially on the same assumptions as Pauling makes. 'The hydrogen fluoride molecule resonates between the two structures $H:\underset{..}{\ddot{F}}:$ and H^+F^-, with the second somewhat more important than the first, so that the bond has somewhat more than one-half ionic character. Similarly the comples ion $[HF_2]^-$ may be considered to resonate among the three structures[16] A, B and C.'

A $:\underset{..}{\ddot{F}}:H\ F^-$

B $F^-\ H^+\ F^-$

C $F^-\ H\ :\underset{..}{\ddot{F}}:$

Pauling's treatment of the bifluoride ion leads to a model with a linear equilibrium configuration of the three ions, with a distance between fluorine atoms of 2·32 A., in good agreement with the experimental value of 2·26 A. ± 0·01. In hydrogen fluoride polymers the distance would be somewhat greater, as in fact the electron diffraction work shows, giving the value 2·55 A. ± 0·05. Briegleb's model, which starts with a Z-shaped dimer,  is either based on a more complex view of hydrogen bonding which may be represented as  involving very complex bonding for further chain development, or it is not based on hydrogen bonding at all.

Further theoretical studies of these competing models have been made. In one case, the application of classical electrostatics led to a Z-shaped model for the dimer,[16] with H - F - F angle 32·5°. It was considered that the best H - F distance to take was 1·007 A., where Briegleb had taken 0·92, the energy values being very sensitive to this interatomic distance. It was calculated for this model that the heat of association to the dimer was 23·9 kg.-cal., in fair agreement with Briegleb's value of 28 ± 3 - 4 kg.-cal. But, as has been seen, Briegleb had later suggested that this value was unreliable, so the argument is inconclusive. Moreover, in this calculation the F - F distance was taken as 2·58 A., as obtained in the electron diffraction work, but this distance was that between two fluorine atoms with a hydrogen atom between them, so that the application of this dimension here seems unjustified. Russian workers[17] have calculated the energy content of two models, one described as a twin, $\mathrm{F-H\ldots F^{H}}$, obviously the hydrogen-bonded chain polymer, the other described as a quadrupole, $\begin{smallmatrix}\mathrm{F} & - & \mathrm{H}\\ & \vdots & \\ \mathrm{H} & - & \mathrm{F}\end{smallmatrix}$, very similar to the Briegleb-Glockler model. It was shown that the twin was energetically the more probable model, and that this would associate further.

Ginell developed mathematically a theory of association of monomeric substances to polymer chains, assuming that the addition of monomer molecules to polymer chains (and the reverse) was the only process of importance, addition of partially polymerized molecules being negligible. The results of the theory were applied to the vapour density determinations of Hildebrand, to calculate the equilibrium constant and thence the heat of reaction. The values first obtained[18] were corrected in a later note.[19] The average value ΔH was 5842 g.-cal. which may be compared with 7406 g.-cal. calculated by alternative treatment, and with $\frac{40{,}000}{6} = 6{,}700$ calculated by Long *et. al.*, above.

The dipole moment of hydrogen fluoride, it has been suggested, should be high relative to those of the other hydrogen halides, because of the tendency to association.[20] Actual measurements on the vapour were carried out, and at pressures such that association was negligible, a mean value of 1·91 Debye units was obtained between 32° and 100°C.[21] Attention was drawn to the identity of this value with Pauling's electronegativity difference, and it was concluded that the hydrogen–fluorine bond in hydrogen fluoride monomer has 43% ionic character, compared with the 60% estimated by Pauling. In this work a series of readings was taken at varying pressures below those at which association began to occur, and the capacity–pressure curve was extrapolated to 760 mm. to give a capacity figure from which the dipole moment of the vapour at 760 mm. could be calculated. In later work, actual measurements at higher pressures were made, and after a preliminary announcement[22] the results were later reported more fully.[23] The dipole moment increases greatly with the pressure, as is shown by the selected values given in Table XIV (fuller data are given in the original paper).

TABLE XIV.- DIPOLE MOMENT OF HYDROFLUORIC ACID VAPOUR (IN DEBYE UNITS)

Pressure mm.	Dipole Moment at given Temperatures, °C.					
	23·1	25·2	31·3	38·5	48·35	59·70
50	1·91	1·91	1·92	1·91	1·92	1·91
250	2·01	1·96	1·96	1·91	1·92	1·91
500	2·36	2·18	2·11	2·03	1·92	1·91
700	2·87	2·70	2·26	2·18	2·00	1·91

It is considered that a ring-form hexamer would have zero dipole moment while Briegleb's model would show dipoles of 0 with an even number of hydrogen fluoride units in the polymer, and 1·91 with an odd number of units. For the high dipole moments found, more or less linear polymers, as indicated by electron diffraction of the vapour and *X*-ray studies of the solid, must be formed. For this model, the dipole moment was in little less than linear proportion to the degree of association. Estimates of the association factor made from the dipole moments obtained were greater than those derived from vapour density measurements. The ratio of these –

$$\frac{\text{association factor from dipole moment}}{\text{association factor from vapour density}}$$

– increased with rising pressure and with falling temperature. It was considered that the best explanation of this difference was the formation of a certain proportion of ring polymers with zero moment: this led to the suggestion that association in hydrofluoric acid vapour consists in the formation of a succession of chain polymers, with appreciable amounts of ring polymers formed from the hexamer. This was again brought out in a later paper,[24] where it was suggested that, from a quantum mechanical point of view, the relation between the polarization measured in these studies and the dipole moment should be given by an equation different from that already used, and that the corrected figure should be 1·98, instead of 1·97 as given by the classical equation. Glockler's version of the Briegleb dimer model is criticised, as it fails to explain the experimental results.

Measurements have also been reported of the dipole moment of hydrogen fluoride in solution in carbon tetrachloride, normal pentane, benzene and 1:4-dioxan (together with other hydrogen halides).[25] It is concluded that the the probable value of the dipole moment for hydrogen fluoride is 1·9 – 2·0 Debye units, and the partial ionic character of the bond is calculated. Positive solvent effects appear, and in dioxan an incipient ionization is shown. The abnormality of hydrogen fluoride and other polar liquids has also been shown by a mathematical treatment of models of the molecules.[26]

Pauling[10] explained the anomalously high melting points and boiling points of ammonia, water, and hydrofluoric acid as being due to hydrogen bonding, and this question has also received further consideration.[27] The properties of the hydrides of the later elements in Groups V, VI and VII of the periodic table were extrapolated to give the 'normal' properties of the elements in the first series, i.e. the properties to be expected if no association occurred. For hydrogen fluoride the following properties were estimated for the unassociated compound

Melting point:	132°K.
Boiling point:	137°K.
Total latent heat of sublimation (Latent heat of melting and evaporation):	3·23 kg.-cal./mole.

Long, Hildebrand and Morell[4] studied the polymerization of deuterium fluoride as well as hydrogen fluoride. Their results, in terms of association factors, are given in Table XV.

There was slightly greater polymerization in the case of the deuterium compound, and the equilibrium constant for the reaction $6DF = (DF)_6$ was given by $\log K = \frac{8970}{T} - 43{\cdot}65$, $\Delta H = -41{,}100$ g.-cal. (300 g.-cal. greater than for hydrogen fluoride). Later, the concentrations of monomeric hydrogen and deuterium fluorides in the vapour were calculated[9] from the determinations already made, and the ratio p_{HF}/p_{DF} obtained. The ratio is greater than

TABLE XV. - ASSOCIATION OF DEUTERIUM FLUORIDE

T, °K	P mm.	z	T, °K.	P mm.	z
273·15	215·3	3·025	305	515	1·493
	203·5	2·881		500	1·470
	191·1	2·720		472	1·385
286	317	2·289		441	1·313
	307	2·219		440	1·322
	292	2·102		439	1·312
	275	1·969		406	1·257
299	447	1·690		354	1·182
	433·5	1·656	311	586	1·340
	412	1·529		567	1·305
	387	1·474		531	1·253
	386	1·472		492	1·205
	386	1·465		491	1·207
	358·5	1·392		489	1·203
	320	1·285		447	1·163
				382	1·118

unity, which is taken to indicate stronger association in the liquid phase for the deuterium than for the hydrogen compound. This behaviour is similar to that of the deuterium and hydrogen compounds in the case of water and ammonia. The data are given in Table XVI.

TABLE XVI. - PARTIAL PRESSURES OF MONOMERIC HF AND DF

T, °K.	Total Pressure			Monomer Pressure		
	P_{HF}	P_{DF}	P_{HF}/P_{DF}	P_{HF}	P_{DF}	P_{HF}/P_{DF}
270	314·0	340·1	0·923	140·7	133·0	1·057
280	468·9	499·5	0·939	232·8	220·5	1·056
290	681·1	714·2	0·953	371·1	351·8	1·055

The effect of hydrogen bonding makes itself felt not only in the association observed in the vapour and in the anomalies of the liquid, but it will be seen also that the behaviour of the aqueous acid is best explained by a reversible polymerization to the dimer stage. Whilst the monomer is a weak acid, the dimer is a stronger monobasic acid, so that the unionized molecule H_2F_2 does not exist in solution, only the ion HF_2^-. Thus the salts formed from this acid, such as KHF_2, are very stable, as shown, for example, by the low partial pressure of hydrogen fluoride over them (see page 24).

The thermodynamics of the system $KHF_2 - KF - HF$ have been examined.[28] The F - F distance, at 2·26 A., is much smaller than the corresponding distance in other hydrogen bonds, and it is shown that the potential energy curve for the proton has a single minimum, half way between the two fluorine atoms, a behaviour that is probably unique. Regarding the HF_2^- ion as one of the most stable structures arising from hydrogen bonding, it has been shown that electrostatic forces are adequate to account for its stability.[29] At an earlier date, an *X*-ray study of the crystal structure of $NaHF_2$ gave a figure of 1·25 A. for the F - F distance,[30] which is higher than the figure now accepted. The solubility of sodium fluoride in aqueous hydrofluoric acid has been determined;[31] the reduction in solubility in the more acid solution is attributed to the formation of bifluoride ion. (The solubility of potassium bifluoride is very much less than that of potassium fluoride.)[32]

On the other hand, the suggestion has been made that ionization to H_2F^+ and F^- may occur,[33] and, in support of this, that complexes with other acids are, *e.g.* $(FH_2)^+ ClO_4^-$; $(FH_2)^+ BF_4^-$; $(FH_2)^+ SO_4H^-$.[34] Later it will be seen that whilst pure hydrofluoric acid has a low conductivity, high conductivity is developed by the addition of many solutes, *e.g.* potassium fluoride. Considering the stability of the ion HF_2^-, there can be little doubt that this conductivity is due to a dissociation: $KF + HF \rightarrow KHF_2 \rightleftharpoons K^+ + HF_2^-$. But if the ion $(H_2F)^+$ could also be formed, hydrofluoric acid itself should be a conductor owing to the dissociation $3HF \rightleftharpoons (H_2F)^+ + (HF_2)^-$, and that this is not so militates strongly against any idea of an $(H_2F)^+$ ion.

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THERMOCHEMISTRY

The heat of formation of hydrofluoric acid from the elements was directly determined by von Wartenburg and Fitaner.[1] A correction was applied for the degree of polymerization of the gas, based on Simons and Hildebrand's data, and a figure obtained, for the heat of formation of monomeric hydrogen fluoride gas, Q_{HF} = 63·0 kg.-cal. From determinations of the heat of reaction of fluorine and sodium chloride, $\frac{1}{2}F_2 + NaCl \rightarrow NaF + \frac{1}{2}Cl_2 + 39{\cdot}3$ kg.-cal., and of the heat of solution of gaseous hydrogen fluoride in water, and other known data, a value Q_{HF} = 65·0 kg.-cal. was obtained by the same workers. A direct determination by Ruff[2] gave 62·3 kg.-cal., but a later paper[3] pointed out an error in von Wartenberg's calculation of the correction for the heat of polymerization, and correcting this, the above figures of 63·0 and 62·3 became 63·8 and 64·2 kg.-cal. Von Wartenberg's value based on the fluorine-salt reaction was criticized because of etching of the glass used; this criticism was not accepted by von Wartenberg, but he thought it desirable to determine the heat of reaction at a temperature where no correction for the heat of polymerization was necessary,[4] and so the measurements were repeated at 100°C. the fluorine being made in a high temperature cell, passed over sodium fluoride to remove hydrogen fluoride and then through a tube cooled in liquid oxygen to remove carbon fluorides and residual traces of hydrogen fluoride. The reaction was carried out in a platinum vessel, and sparking was necessary to ensure reaction. The specific heat correction from 20° to 100° was estimated to be negligible, and the final value was Q_{HF} = 64·45 ± 0·1 kg.-cal., which, it was pointed out, was the mean of the previous direct values and that based on the sodium chloride reaction. Attempts have been made to obtain a value for the heat of formation from *E.M.F.* measurements. Simons and Hildebrand tried to measure the potential of a H_2/F_2 cell but were unsuccessful because, in a solution of potassium fluoride and hydrogen fluoride, graphite disintegrated and they were unable to find a metal suitable for use as a fluorine electrode.[5] Morgen and Hildebrand measured the decomposition voltage of fused potassium bifluoride, and calculated a value Q_{HF} = 33.6 kg.-cal.;[6] the voltages measured were obviously far too low, however, being about 1.5V. A break at about this figure has been observed in the electrolysis of aqueous fluoride solutions (see p. 133) and has been attributed to the decomposition of water. Fredenhagen and Krefft[7] bubbled hydrogen and fluorine over platinized platinum electrodes immersed in anhydrous hydrofluoric acid at 0°, a little potassium fluoride being added; the voltage of this primary cell was 2.768, whence a value of Q_{HF} = 62·63 kg.-cal. was calculated, in very fair agreement with the direct value. The heat of activation in the reaction of hydrogen and fluorine has been discussed.[8] Efforts have been made to determine the dissociation energy. An early value, based on quantum considerations, of 33·3 kg.-cal. was anomalous; the same method gave 316·5 for fluorine.[9] Later, from consideration of band spectra, a value of 172 kg.-cal. was obtained.[10] Taking $D_{H_2} = -103$, $D_{F_2} = -38$, and $Q_{HF} = 64$, the value for D_{HF} is −135 kg.-cal.

In discussing the association of hydrogen fluoride reference has already been made to the ionic character of the valency bond, and further consideration has been given to Pauling's views on this question.[11] The polar character of the bond has been adduced to explain the observed exchange between fluorine and hydrogen fluoride,[12] which is less than with chlorine and hydrogen chloride. In the latter case the exchange is a rapid and homogeneous reaction through the formation of an intermediate complex HCl_3, whereas the polarity of the H–F bond tends to keep the one fluorine atom distinguished from the others in any such complex and therefore reduces the possibility of fluorine exchange. The bond lengths in the hydrogen halide molecules have been calculated by the valency bond method;[13] they are all shorter than the sum of the covalent radii, and the contraction is greatest in the case of hydrogen fluoride, again because the bond is more ionic in character. Further examples of the influence of this ionic character have been cited.[14,15] The energetics of the hydrogen fluoride molecule, in comparison with neighbouring hydrogen compounds, has been considered.[16,17] The relation between effective diameter and molecular structure in the series Ne-HF-H_2O-NH_3-CH_4 has been studied[18] and the data of band spectroscopy applied to establish the internuclear distance, with the force constants, for hydrogen fluorides and other hydrides.[19] This question is further pursued under spectroscopy (see page 218).

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PHYSICAL PROPERTIES OF AQUEOUS SOLUTIONS.

Freezing points in the aqueous hydrofluoric acid system have been determined:[1] the results are shown in Fig. 3, and the data are given in Table XVII.

TABLE XVII. - FREEZING POINTS OF AQUEOUS HYDROFLUORIC ACID

HF mole fraction	Temp. °K.	Solid Phase	HF mole fraction	Temp. °K.	Solid Phase
0·00777	272·10	ice	0·698	197·6	$H_2O.2HF$
0·0564	266·7	ice	0·710	197·3	$H_2O.2HF$
0·0809	263·2	ice	0·743	191·3	$H_2O.2HF$
0·1565	250·0	ice	0·762	181·9	$H_2O.2HF$
0·216	231·6	ice	0·776	171·7	eutectic
0·265	213·0	ice	0·786	172·3	$H_2O.4HF$
0·276	202·9	eutectic	0·796	172·7	$H_2O.4HF$
0·307	210·3	$H_2O.HF$	(0·800)	(172·8)	$H_2O.4HF$
0·321	213·6	$H_2O.HF$	0·817	172·4	$H_2O.4HF$
0·371	224·1	$H_2O.HF$	0·864	167·6	$H_2O.4HF$
0·403	229·5	$H_2O.HF$	0·883	162·2	eutectic
0·478	236·9	$H_2O.HF$	0·894	166·1	HF
(0·500)	(237·7)	$H_2O.HF$	0·913	173·3	HF
0·515	237·2	$H_2O.HF$	0·939	179·4	HF
0·575	231·5	$H_2O.HF$	0·961	184·1	HF
0·627	222·0	$H_2O.HF$	0·974	186·1	HF
0·675	204·9	$H_2O.HF$	0·982	187·6	HF
0·685	197·9	$H_2O.HF$ and $H_2O.2HF$	1·000	190·1	HF

Data were given earlier for the more dilute end of the system up to 8% hydrogen fluoride,[2] and some of these are given in Table XVIII.

TABLE XVIII. - FREEZING POINT LOWERING IN DILUTE HYDROFLUORIC ACID

Moles HF/1000 g.H_2O.	0·02	0·04	0·06	0·08	0·10	0·25	0·50	0·80	1·00
f.p. lowering, °C.	0·043	0·083	0·122	0·160	0·199	0·482	0·949	1·507	1·880

The activity of ionic species as calculated from these results is considered later. It is seen that three compounds are formed, of which $H_2O.HF$ had been previously identified, with a reported melting point of -35°C. compared with -35·4° in this work. The second compound, $H_2O.2HF$, not so clearly defined, is new, as is the third, $H_2O.4HF$, with a melting point of -100·4°C. It is pointed out that the existence of two compounds with an excess of hydrogen fluoride, whilst there are none with an excess of water, harmonizes with the view that hydrogen fluoride tends to a more complex polymerization than does water. The existence of a compound $HF.9H_2O$, suggested in the original work (Mellor, II, 131), was not confirmed. Evidence for the existence of the compound $H_2O.2HF$ has also been found in a function derived from the density.[3]

The densities of solutions up to 54% hydrogen fluoride are given in Table XIX.[4]

TABLE XIX. - DENSITIES OF AQUEOUS HYDROFLUORIC ACID

wt. % HF	5·06	10·1	15·3	20·25	26·4	29·8	36·4	39·9	42·4	47·3	48·4	53·8
d_{15} g./cc.	1·017	1·035	1·054	1·072	1·097	1·1085	1·134	1·149	1·1595	1·179	1·183	1·205

The author points out that in the earliest results previously available, those of Eckelt (1898), there was complete absence of experimental details. Winteler (1902) worked in platinum and obtained results in good agreement

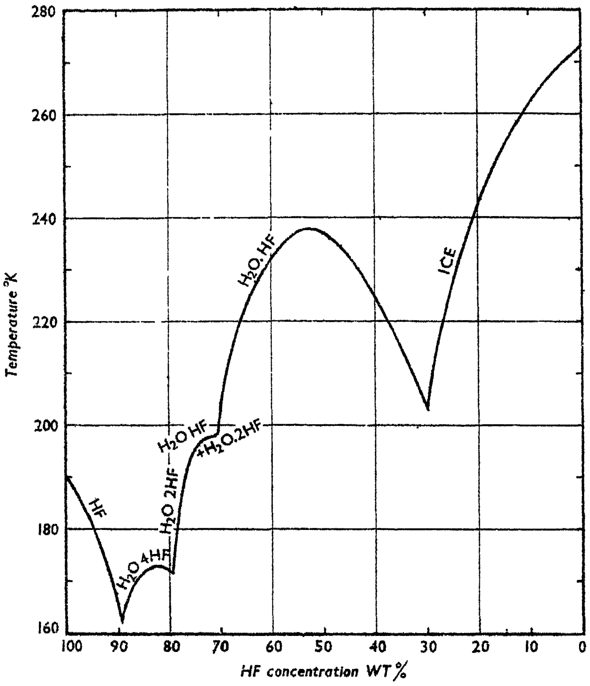

Fig. 3. FREEZING POINTS OF AQUEOUS HYDROFLUORIC ACID SOLUTIONS

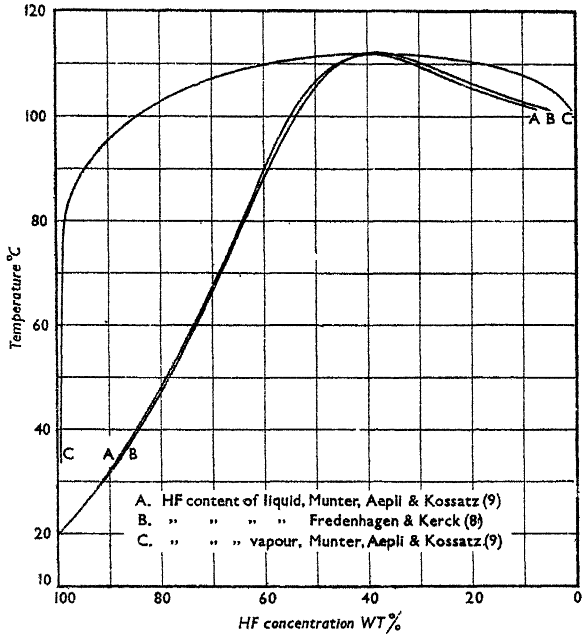

Fig. 4. BOILING POINTS OF AQUEOUS HYDROFLUORIC ACID SOLUTIONS AND COMPOSITION OF THE VAPOUR

with the above up to a concentration of 30%, but found appreciably lower values at higher strengths. In obtaining the above data, a special dense bakelite vessel was used and care was taken to show that it was constant in weight and inert to hydrofluoric acid. The acid used was made from Frémy's salt and was of high purity.

The magnetic rotation of hydrofluoric acid (39%) has been determined in a fluorspar vessel. The molecular magnetic rotation for hydrogen fluoride, calculated from these determinations, is $1{\cdot}30 \times 10^{-5}$, which is less than that of all other substances except neon and possibly helium.[5] The *X*-ray absorption of 8N. solutions of hydrofluoric acid has been determined, but gives no indication of the structure.[6]

A number of results on the boiling points and vapour pressures of aqueous hydrofluoric acid have been published. In an early result[7] the composition of the constant boiling mixture was given as 38•18% hydrogen fluoride and the boiling point as 110•8°C. at 732 – 735 mm. of mercury, the density of this acid at 20°C. being 1•138 g./c.c.; later results give slightly different values, 111•35° at 35•64% and 760 mm;[8] 112•0° at 38•26% and 750 mm.[9] The boiling point-composition data of Fredenhagen and Wellmann[10] have been criticized, and as in a later paper by Fredenhagen and Kerck[8] very different results are given, the earlier results may perhaps be ignored. It is said that in the region of 55 to 80 mol. % of hydrogen fluoride it was difficult to attain steady boiling: superheating of the whole liquid to as much as 20° above the boiling point occurred, steady boiling could be secured only by very careful heating, and even then the boiling point varied as much as 1°. It is in this region that the greatest differences from the earlier results of Fredenhagen and Wellmann were observed. The results are given in Table XX.

TABLE XX. - BOILING POINTS OF HYDROFLUORIC ACID SOLUTIONS

Moles H_2O/1000g.HF	667	384	204	164	154	138	113	100	73
Mole % HF	6•98	11•52	19•70	23•32	24•46	26•63	30•62	33•26	40•48
b.p. °C.	101•45	102•83	106•05	107•55	108•60	108•80	110•93	111•34	111•10
Moles H_2O/1000g.HF	66•1	53•8	45•0	39•7	35•0	31•3	25•7	24•7	20•85
Mole % HF	43•08	48•19	52•66	55•78	58•86	61•51	66•09	66•99	70•39
b.p. °C.	109•90	106•00	100•6	85•5	79•5	86•5	74•6	68•5	62•3
Moles H_2O/1000g.HF	18•05	12•88	10•93	6•01	5•64	4•72	4•5	4•0	3•5
Mole % HF	73•48	79•55	82•07	89•28	89•87	91•38	91•80	92•06	93•04
b.p. °C.	58•5	44•5	46•05	32•12	28•3	29•5	28•95	27•92	26•89
Moles H_2O/1000g.HF	3•0	2•5	2•0	1•5	1•0	0•75	0•5	0•4	0•3
Mole % HF	94•03	95•02	96•01	97•00	98•00	98•50	99•00	99•20	99•40
b.p. °C.	25•9	24•89	23•88	22•87	21•86	21•14	20•81	20•58	20•35
Moles H_2O/1000g.HF	0•2	0•1	0•05	0					
Mole % HF	99•64	99•82	99•91	100					
b.p. °C.	20•10	19•84	19•70	19•54					

A series of observations has been made by Russian workers of the partial pressures of water and hydrofluoric acid vapours over various solutions and at various temperatures,[11] and the results are given in Table XXI.

The partial pressures of water and hydrogen fluoride at different temperatures and for acid strengths up to 29•7% have been expressed in the following equations where *w* = weight per cent. of hydrogen fluoride in solution.[12]

$$25°\text{C.},\ \log(p_{HF} + 0{\cdot}172) = -0{\cdot}72956 + 0{\cdot}031541w \text{ and}$$
$$\log(34{\cdot}14 - p_{H_2O}) = 1{\cdot}00817 + 0{\cdot}010473w$$

$$40°\text{C.},\ \log(p_{HF} + 0{\cdot}455) = -0{\cdot}31390 + 0{\cdot}03489w \text{ and}$$
$$\log(70{\cdot}95 - p_{H_2O}) = 1{\cdot}20161 + 0{\cdot}013532w$$

Refs. p. 110.

$$60^\circ\text{C., } \log(p_{HF} + 1{\cdot}465) = 0{\cdot}18759 + 0{\cdot}033478w \text{ and}$$
$$\log(212{\cdot}1 - p_{H_2O}) = 1{\cdot}7957 + 0{\cdot}01029w$$
$$75^\circ\text{C., } \log(p_{HF} + 3{\cdot}012) = 0{\cdot}50190 + 0{\cdot}033194w \text{ and}$$
$$\log(368{\cdot}3 - p_{H_2O}) = 1{\cdot}9076 + 0{\cdot}013475w$$

TABLE XXI. - PARTIAL PRESSURES OF H_2O AND HF OVER AQUEOUS ACID

Temp. °C.	Concentration HF		p_{HF} mm.	p_{H_2O} mm.	p_{total} mm.
	wt. %	mol. %			
25	19·00	17·42	0·53	14·9	15·43
	27·60	25·56	1·37	10·0	11·37
	39·20	36·70	5·59	10·1	15·70
40	5·00	4·52	0·11	49·5	49·51
	10·00	9·09	0·53	44·9	45·93
	12·85	11·65	0·82	43·7	44·52
	19·00	17·42	1·20	39·1	40·30
50	5·00	4·52	0·21	83·0	83·21
	10·00	9·09	0·86	76·9	77·76
	12·85	11·65	1·57	68·6	70·17
	19·00	17·42	2·48	57·6	60·08
	27·60	25·56	6·50	41·0	47·50
	39·20	36·70	22·14	34·0	56·14
60	5·00	4·52	0·49	131·5	131·99
	10·00	9·09	1·52	117·6	119·12
	19·00	17·42	4·63	104·0	108·63
	27·60	25·56	10·61	72·7	83·31
75	5·00	4·52	1·97	267·0	268·97
	10·00	9·09	3·78	244·3	248·08
	12·85	11·65	6·35	237·6	243·95
	12·85	11·65	5·65	243·0	248·65
	19·00	17·42	9·69	207·9	217·59
	19·00	17·42	10·66	210·0	220·66
	27·60	25·56	24·39	153·3	177·69

The results were obtained by the dynamic method, dry air being saturated with vapour over a solution of known composition and then passed through an absorption train so that the amounts of hydrogen fluoride and water could be determined. The authors do not say how the weights so obtained were converted to partial pressures; if this involved the assumption of perfect gas behaviour, some demonstration of the validity of the assumption would be desirable even though the partial pressures were low. The liquid–vapour equilibrium at the normal boiling point over the whole range of compositions has been determined[9] using an equilibrium still method, and in this case the vapour composition is given as a percentage by weight of the constituent. The results are given in Table XX, the normal boiling point being the corrected figure at 760 mm., from the observed boiling point and barometric pressure.

The boiling points are plotted in Fig. 4, together with those of Fredenhagen and Kerck referred to in Table XXII. The authors have later reported the vapour compositions at lower temperatures,[13] determined by the dynamic method: on plotting log p against $1/T$ the results give good straight lines which extrapolate to the figures given in Table XXII for the composition at the normal boiling point. Expressing the data in the form of equations,

$$\log p_{mm} = B - \frac{A}{T}$$

the values of the constants A and B at different strengths are given in Table XXIII.

TABLE XXII. - LIQUID AND VAPOUR COMPOSITIONS AT THE NORMAL BOILING POINT FOR HYDROFLUORIC ACID.

Normal b.p. °C.	Composition, wt. %HF	
	Liquid	Vapour
101·6	5·47	0·87
102·8	10·1	2·03
106·8	20·6	7·06
108·4	24·7	11·6
110·3	30·1	19·4
111·7	36·2	32·8
112·0	36·8	34·4
112·1	37·6	36·4
112·3	38·22	38·15
112·4	38·27	38·26
112·1	39·2	41·1
111·4	42·2	50·1
108·7	47·0	65·7
106·8	49·2	–
101·7	52·9	82·6
98·9	54·8	87·4
90·9	58·6	92·9
86·6	60·7	97·3
79·0	64·1	99·0
74·6	66·2	98·7
61·6	72·0	98·8
45·1	81·4	99·3
33·5	89·0	99·5

TABLE XXIII. - CONSTANTS IN THE PARTIAL PRESSURE EQUATION

$$\log p_{\mathrm{mm}} = B - \frac{A}{T}$$

Liquid wt. %HF	p_{HF}		$p_{\mathrm{H_2O}}$	
	$A \times 10^3$	B	$A \times 10^3$	B
10	2·610	8·043	2·225	8·794
20	2·605	8·496	2·235	8·742
30	2·500	8·632	2·247	8·661
50	2·120	8·324	2·386	8·613
70	1·830	8·314		

The authors point out that the vapour pressures for water in the 70% acid are less reliable as this is the limiting concentration which can be studied by this method. They note that their results are lower than those of Fredenhagen and Wellmann, and when plotted on a semilogarithmic scale against $1/T$ are more regular, and somewhat greater, than the results of the Russian workers reported above.[11] The results are also rather lower than the values for 10 and 20% solutions calculated from the work of Brosheer *et al.*[12] though at 30% the agreement seems good. The relation between the partial pressure of hydrofluoric acid in the vapour and the acid strength at different temperatures has been expressed in the form of a nomogram (Fig. 5)[14] based on the results of Brosheer *et al.*[12] and others.[15] A mechanism for the formation of azeotropes of the type of hydrofluoric acid has been suggested,[16] and a theory relating the vapour pressure curves to volume changes on mixing and to heat of mixing has been proposed.[17] Attention may be drawn here to the determination of liquid–vapour compositions in the system comprising aqueous hydrofluoric and hydrofluosilicic acids[9,11] which will be dealt with more fully under Silicon.

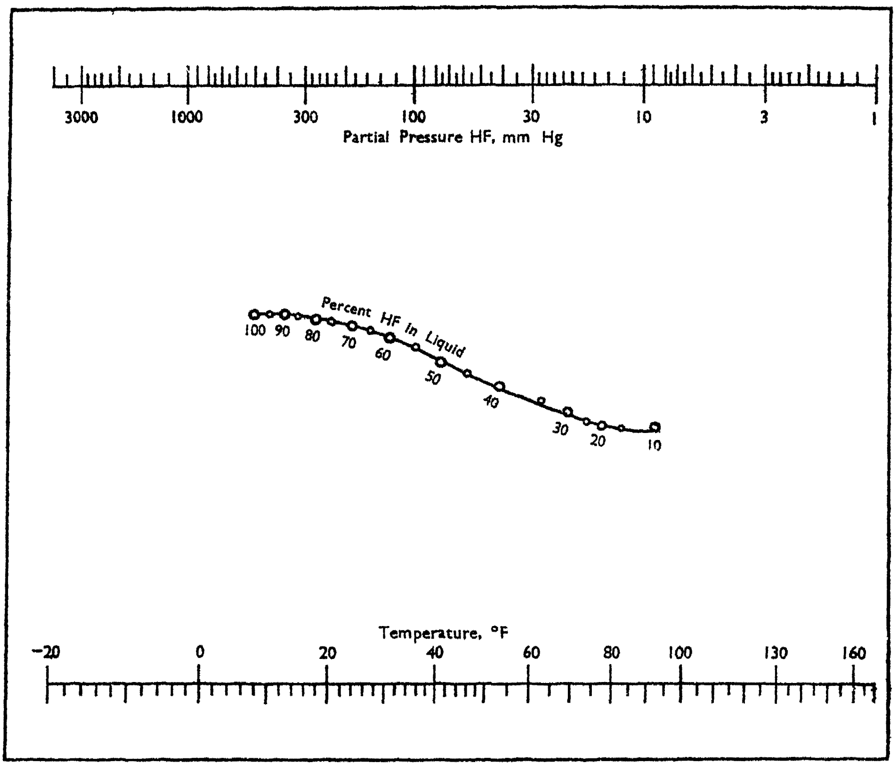

Fig. 5. NOMOGRAM FOR VAPOUR PRESSURE OF HF OVER AQUEOUS HYDROFLUORIC ACID SOLUTIONS

The following determinations of specific heat have been reported.

(1) Mulert, reported by Mellor (II, 131):

wt.%HF	5.0	7.51	13.26	20.0	25.92
sp. ht.	0.947	0.925	0.875	0.840	0.798

(2) Ray:[18]

wt. %HF	10	20	30	34.6
sp. ht.	0.908	0.838	0.756	0.724

The acid used had 34.6% HF, 0.88% SiO_2; weaker acids were made by dilution of this.

(3) Roth and Chall:[19] 20.99% HF (HF + 4.181 H_2O)

at 50°C. sp. ht. 0.8719 g.-cal./g.
20°-50°C. sp. ht. 0.8653 g.-cal./g.

(4) Pranschke and Schwiete:[20] true specific heats at 18° ± 1

wt. %HF	9·81	20·1	32·8	40·7
sp. ht.	0·914	0·856	0·801	0·768

(5) Roth and Becker:[21] true specific heats at temperatures between 19·2 and 20·4°C.

wt. %HF	0·2077	1·043	1·720	5·146	10·237	19·827
sp. ht.	0·9952	0·9875	0·9832	0·9590	0·9148	0·8607
t °C.	19·7	19·2	20·0	19·4	19·2	20·4

(6) Roth *et al.*[22] give interpolated results at 20°C. based on (5).

(7) Thorvaldson and Bailey:[23] mean specific heats, 18 – 20°C.

wt. %HF	0·551	1·086	1·459	2·173	5·26	10·02	14·96	19·97	25·10	34·95	48·13
sp. ht.	0·9956	0·9919	0·9882	0·9824	0·9596	0·9258	0·8917	0·8603	0·8294	0·7734	0·7185

The last determinations, made with an acid of high purity, were carried out with great care. The authors comparing their results with (1), (2), and (4) above, but, surprisingly, not with those of Roth, found that (1) and (2) were rather similar but about 3% low at 10% HF and 6% low at 30% HF, whilst (4), in agreement at 25% HF, was 1·3% low at 10% and 2·9% high at 40% HF. They remarked that in most cases insufficient details of experimental methods and results were given. The results of (5) are in better agreement though in general a little lower, the average difference being 0·38%. It is interesting to note that the results of Roth and Becker, not having been published in any scientific journal, are not cited in the abstract journals and are therefore lost

TABLE XXIV. - HEAT OF DILUTION OF HYDROFLUORIC ACID

N	Heat of Dilution (g.-cal./g.-mol)	
	from N = 1·796	to N = 500
2	+75	+573
3	280	368
4	376	272
5	430	218
7·5	480	168
10	502	146
15	523	125
20	529	119
30	536	112
40	542	106
50	551	97
75	562	86
100	570	78
150	585	63
200	598	50
250	606	42
300	617	29
400	633	16
500	648	± 0
600	665	–17
700	681	–33
800	702	–54
900	726	–78
1000	752	–104
1100	780	–132
1200	812	–164
1300	866	–218
1400	910	–262

sight of, appearing first in a reference book, Landolt-Börnstein. Enthalpy diagrams have been prepared using published data, that of Vogt[24] based on the data of Roth *et al.*, that of Tyner[25] based on the results of Thorvaldson and Bailey.

Heats of dilution of aqueous hydrofluoric acid are given in Table XXIV.[22] The original acid had 38·22% hydrofluoric acid, *i.e.* N = mols H_2O/20 g. HF = 1·796. When this acid was diluted to the value of N given in the first column the heat evolved per 20 g. of hydrofluoric acid at 20°C. was that given in the second column, and the calculated value for the heat evolution on diluting from the first column value to N = 500 is given in the third column.

The heat of neutralization has also been determined.[26] For different dilutions (N = moles H_2O/20 g. HF) neutralised with 0·2659 normal, caustic soda at 19·5 – 19·7°C. the results were

N	4·491	548	1064
H, kg.-cal./20 g.	17·16	16·86	16·73

Some further results are given later (pages 116,118).

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DISSOCIATION OF AQUEOUS SOLUTIONS

The dissociation of hydrofluoric acid in aqueous solution does not follow a simple course. Ostwald's Dilution Law, which often very exactly relates the ionization, as estimated from the conductivity of weak electrolytes, and the concentration, in terms of the law of mass action, fails in this case. The value of K calculated from $\frac{\lambda_v^2}{\lambda_\infty(\lambda_\infty - \lambda_v)V}$ is in many cases constant over a wide range of concentrations, but this is not so for hydrofluoric acid. In this case the value of K calculated from the conductivity falls as the dilution increases, and it has been said that no other acid offers any analogy.[1] This behaviour was discussed by Mellor in the original Treatise (II, 132), and it appeared that the proposal advanced by Pick in 1912 offered an explanation. The equilibrium constant calculated from the conductivity results of Deussen did appear to reach constancy at high dilutions, and the higher values obtained from less dilute solutions were attributed to the onset of another reaction, $HF + F^- \rightleftharpoons HF_2^-$. At high dilutions this equilibrium lies entirely over to the left and, the ions present being then preponderantly hydrogen and fluoride, the equilibrium constant for the reaction $HF \rightleftharpoons H^+ + F^-$ can be determined from the conductivity data. Pick gave a figure of $7{\cdot}2 \times 10^{-4}$ for this constant at 25°C., and showed that by taking a value for the equilibrium constant of the second reaction,

$$\frac{[HF_2^-]}{[HF][F^-]} = 5{\cdot}2$$

he could account for the conductivities observed. Auméras redetermined the conductivity, however, and could find no constancy in the value of K at high dilutions.[2,3] He suggested that the contamination of the acid used in the earlier experiments with hydrofluosilicic acid, as admitted by Ostwald, might account for the difference between his results and Pick's. Further determinations by Fredenhagen and Wellmann[4] gave values of K fitting nicely between those of Ostwald and of Deussen but, at higher dilutions than previously reported, showing a continued steady decline. Later work by Roth[1] gave rather a smaller rate of decrease of K at intermediate concentrations so that the approach to a constant value of K was not so good as in some of the earlier work. Irregularities were observed in dilutions greater than 5000 l./g.mole. Fig. 6 shows the results of these workers on the variation of K with $\log_{10} v$, (where v is the dilution, in litres per g.-equivalent). In this figure are also shown the results of Hill and Sirkar[5] which were obtained at 18°, most of the others being at 25°, but this temperature difference would not account for these extremely low values. Two curves of Roth's are given, for 18° and 20°C. Although the logarithmic plot drastically shortens any plateau on the right hand end of the curve and exaggerates the later rate of decline in Fredenhagen and Wellmann's results, it shows up the general lack of agreement. Even though it may be suggested that in the most widely varying results some serious error must have occurred, there is still considerable scatter amongst the other data. No explanation is available of the greater or the lesser variations shown. In the conductivity data on which this diagram is based, those of Ostwald and of Deussen are as re-calculated by Fredenhagen and Wellmann, those of Hill and Sirkar are as given in Landolt-Börnstein. The equivalent conductivities from which K has been calculated are given (for the later workers only) in Table XXV.

The problem has been investigated from other angles also. Hudleston and Davies[6] measured the transference numbers of the ions in various strengths of hydrofluoric acid, and writing a series of equations for the various molecular species present, were able to solve these equations by using also existing

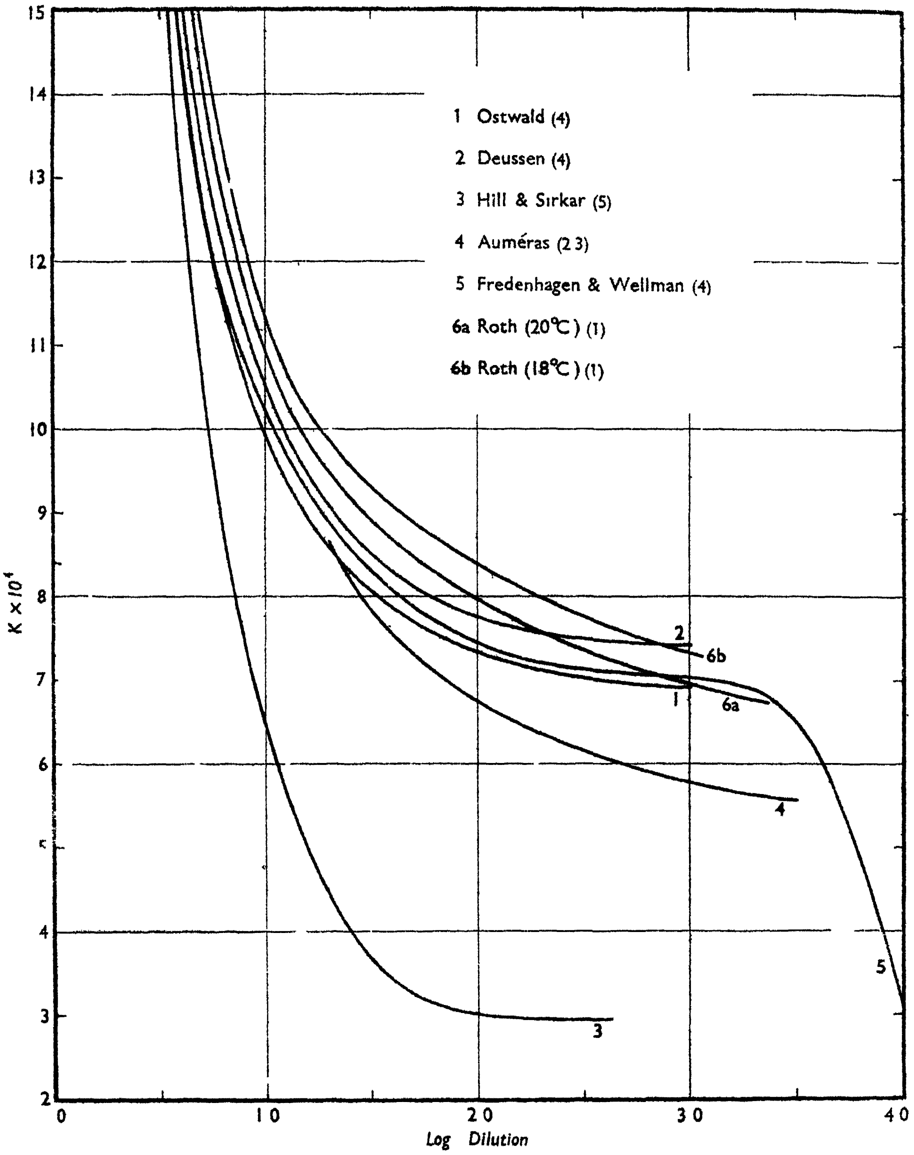

Fig. 6. EQUILIBRIUM CONSTANTS FOR DISSOCIATION OF AQUEOUS HYDROFLUORIC ACID SOLUTIONS (FROM CONDUCTIVITY DATA)

TABLE XXV. - VARIATION OF EQUIVALENT CONDUCTIVITY WITH CONCENTRATION OF AQUEOUS HF

Hill and Sirkar[5]		Auméras[2,3]		F. and Wellmann[4]		Roth[1]			
t = 18°C.		t = 25°C.		t = 25°C.		t	16°	18°	20°
v	Λ	v	Λ	v	Λ	v	Λ	Λ	Λ
0·061	20·7								
0·075	21·3								
0·119	22·1								
0·251	24·2								
0·410	24·3			0·5	21·25				
0·799	25·1			1·0	23·77				
1·32	26·2			10	38·4				
4·12	27·7			100	95·3	4·33	28·12	28·71	29·29
8·24	29·9	20	49	1000	223·0	5·72	30·31	30·86	31·40
16·5	34·6	25	53	2000	269	10·48	36·31	36·90	37·51
33·0	40·5	33	59	3000	393	13·39	40·09	40·63	41·18
65·9	52·7	50	70·5	4000	306	15·43	41·75	42·51	43·28
132·0	65·9	100	90	5000	310	32·4	56·96	58·08	59·21
264	100·2	300	138	6000	320	63·8	73·64	75·04	76·40
527	131·8	1000	209	8000	319	176·1	111·38	113·29	115·23
		3000	279	10000	325	416·5			155·4
						1139		212·2	216·0
						2345			259·9
						∞	350·5	361·9	374·4

conductivity data (Deussen's). They obtained the results shown in Table XXVI.

TABLE XXVI. - COMPOSITION OF HYDROFLUORIC ACID SOLUTIONS (HUDLESTON AND DAVIES, 1924)

Dilution, v	0·5	1	2	4	8	16	32
$[F^-]$ g.-mols/l.	0·0118	0·0113	0·0104	0·0089	0·0072	0·0055	0·0040
$[H^+]$ g.-mols/l.	0·1118	0·0588	0·0319	0·0184	0·0112	0·0072	0·0048
$[HF_2^-]$ g.-mols/l.	0·0999	0·0475	0·0215	0·0094	0·0040	0·0018	0·0008
$[HF]$ g.-mols/l.	1·7883	0·8937	0·4466	0·2222	0·1098	0·0535	0·0257
K_2	4·72	4·72	4·65	4·75	5·03	6·05	7·30

In this work $K_1 = \frac{[H^+][F^-]}{[HF]}$ was taken as $7{\cdot}4 = 10^{-4}$, and the value of $K_2 = \frac{[HF_2^-]}{[HF][F^-]}$ hardly shows a satisfactory constancy. The mobility of the HF_2^- ion was about 75. Arising from this work, the freezing point lowering was determined[7] and found to agree with the solution composition previously calculated.

Auméras, as has been seen above, could not obtain any constant value for K. He used a chemical method, the influence of strong acids on the solubility of calcium fluoride, to determine K_1, and thus found $1{\cdot}67 \times 10^{-4}$ at 25°C., very different from Pick's[8] $7{\cdot}2 \times 10^{-4}$. He showed, however, that if complex formation in aqueous solutions led to the formation of HF_2^- ions, his chemical method would mask this equilibrium if the equilibrium constant for complex formation, K_2 above, were less than 20.[3]

Numerous methods have been used to determine, or estimate, the hydrogen ion activity or concentration. Hudleston and Wynne-Jones determined the e.m.f. of a hydrogen electrode in various strengths of acid;[9] the activity of hydrogen calculated from the results was greater than the hydrogen ion concentrations calculated by Hudleston and Davies[6] in acids stronger than 0·4N; this anomaly was possibly due to an error in a liquid junction potential. The activities in higher concentrations of acid were determined from measurements of e.m.f.s against a quinhydrone electrode by other workers.[10]

Molality m, g.-moles HF/1000 g. solution	3·485	33·5
Activity of hydrogen ion, a_{H^+}	0·3715	6·0
Activity coeff. $\gamma = a_{H^+}/m$=degree of dissocn.	0·106	0·179

These results are in stronger acids than concern the present discussion. Roth, whose conductivity studies have already been referred to, also used an indicator method for the determination of hydrogen ion concentrations.[11] For these essentially visual studies the vessels and the technique to be employed presented a problem. In calorimetric work on aqueous hydrofluoric acid it had been found that waxed glass was not completely satisfactory as there was slight penetration of the wax and attack on the glass. The indicator studies were therefore carried out in platinum and observations were made by reflected light. The hydrogen ion concentrations at 19°C. were in very good agreement with those determined by Hudleston and Davies at 25°C. and given in Table XXVI above. The work was later repeated more accurately,[1] but this time using transparent vessels of 'Plexiglas', a polymethyl methacrylate product available commercially which resisted hydrofluoric acid very satisfactorily and with which it was possible to use transmitted light. The indicators used were methyl-violet, Tropaeolin OO and other similar compounds, and an interesting demonstration was given of the strong temperature dependence of the dissociation. If a very dilute solution, coloured with the indicator, was heated to 30° in a tube the lower end of which was cooled in ice, a clear difference in colour between the upper and the lower end was observed, the cooler end being more acid.

The results, variously referred to as hydrogen ion activities and hydrogen ion concentrations, and now given at 15° and 25°C. were again in fair agreement. Roth calculated the value of K from these results, assuming (as in the calculation of K from conductivities) that the only species to be considered were H^+, F^- and HF. In this case

$$K = \frac{(a_{H^+})^2}{(m - a_{H^+})} \quad \text{where } m \text{ is the molality.}$$

The results are given in Table XXVII together with the earlier results obtained at 19°C. (molalities having been converted to dilutions, v).

TABLE XXVII. - HYDROGEN ION CONCENTRATIONS BY INDICATOR METHOD

1937				1939			
	19°C.			15°C.		25°C.	
v	$[H^+]$	10^4K_1	v	a_{H^+}	10^4K_1	a_{H^+}	10^4K_1
0.942	0.061	37	1.788	0.0406	31.8	0.0338	21.7
1.082	0.046	24	5.040	0.0191	20.4	0.0168	15.5
2.08	0.031	21	8.139	0.0120	13.0	0.0106	10.0
3.91	0.016	11	11.79	0.0092_2	11.2	0.0074_3	7.1_3
7.50	0.011	10	19.37	0.0060_0	7.8_6	0.0050_5	5.46
11.4	0.0080	8	63·69	0.0026_3	5.2_9	0.0022_2	3.66
18.6	0.0056	6.5	93.26	0.0020_1	4.6_2	0.0016_4	2.96
33.4	0.0035	4.8					

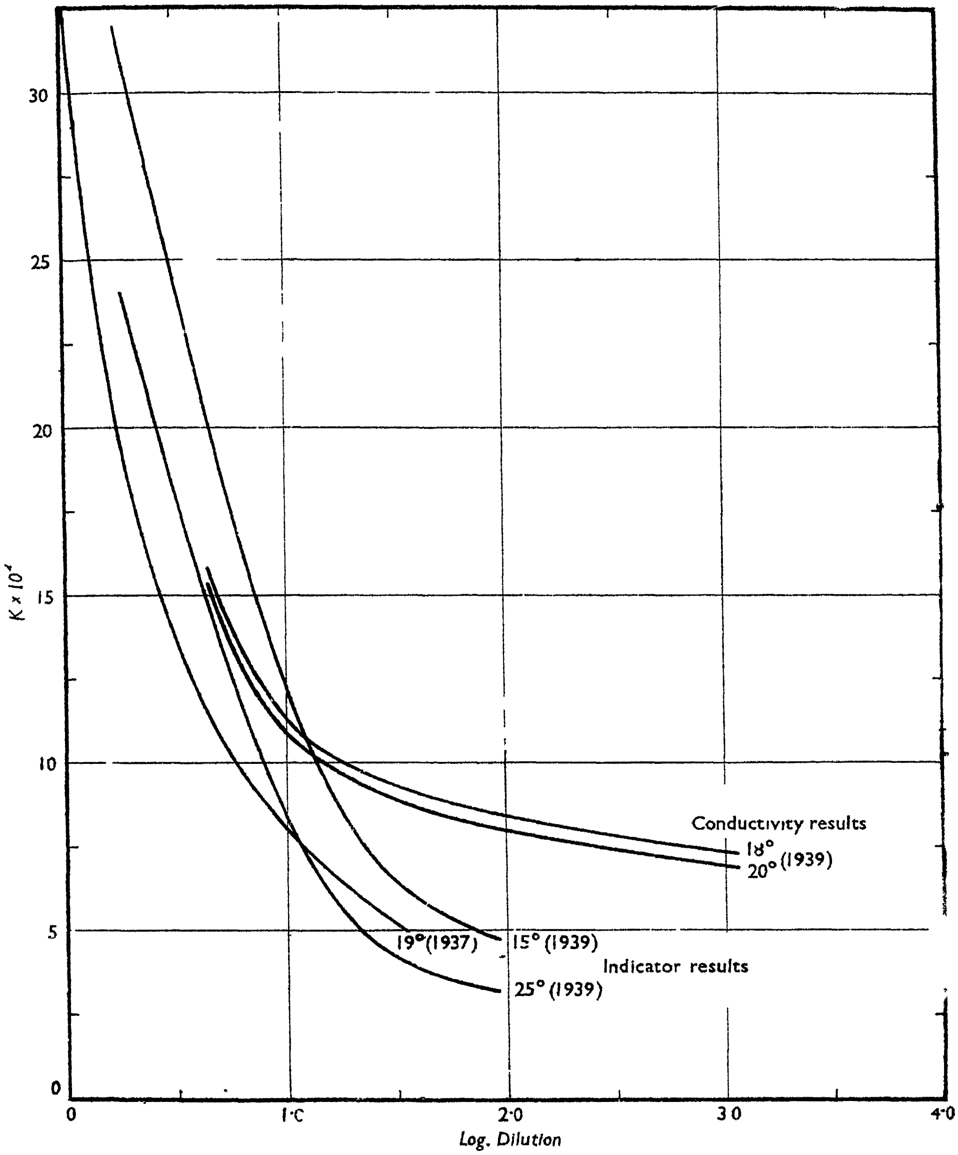

Fig. 7. EQUILIBRIUM CONSTANTS BY INDICATOR METHOD AND CONDUCTIVITY METHOD COMPARED

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The values of K are plotted in Fig. 7 and Roth's values for K from the conductivity are also shown. There is as little tendency for the later results to approach constancy as there is for the conductivity values, and there is no agreement between the two sets of results.

Among later results, it has been stated[12] without any experimental details, that in connection with the experimental work on the dissociation of aluminium fluoride, the following equilibrium constants were calculated from potentiometric measurements at 25°C.

$$\frac{a_{\mathrm{H^+}} \times a_{\mathrm{F^-}}}{C_{\mathrm{HF}}} = 6{\cdot}9\times 10^{-4}; \qquad \frac{a_{\mathrm{HF_2^-}}}{C_{\mathrm{HF}} \times a_{\mathrm{F^-}}} = 5{\cdot}4;$$

and from measurements at constant ionic strength,

$$\frac{C_{\mathrm{H^+}} \times C_{\mathrm{F^-}}}{C_{\mathrm{HF}}} = 1{\cdot}22\times 10^{-3}; \qquad \frac{C_{\mathrm{HF_2^-}}}{C_{\mathrm{HF}} \times C_{\mathrm{F^-}}} = 4{\cdot}8$$

Measurements have been made[13] of e. m. f.s of cells of the type $Pb(Hg)|PbF_2(s)|HF(m_1)|NaF(m_2)|H_2(g)$: and $Pb(Hg)|PbF_2(s)|HF(m)|H_2(g)$. From the results, equations were obtained relating possible values of Pick's equilibrium constants, K_1 and K_2 and hydrogen ion activities q, and by inserting numerical values of q, a plot relating K_1 and K_2 was obtained. For four different solutions, four different lines were obtained at each temperature, which should intersect in one point giving the actual values of K_1 and K_2. There are six possible intersections and these, in the example given, are rather widely spread. The values preferred by the authors are:

	15°	25°	35°
$10^4 K_1$	7·93 ± 0·10	6·71	5·64
K_2	3·94 ± 0·10	3·86	4·32

Results are also given for activity coefficients of hydrofluoric acid at these temperatures and over a range of concentrations. The term 'unilateral triple ion formation' has been used to describe the case where a single ionic equilibrium of the type $B^- + AB \rightleftharpoons AB_2^-$ is superposed on the simple ionization of AB, this being distinguished from the case in which the equilibrium $A^+ + AB \rightleftharpoons A_2B^+$ also occurs.[14] The data of Hudleston and Davies were subjected to further analysis and correction, and their conclusions confirmed. Using Deussen's conductivity data, and introducing activity and mobility coefficients, the following values of the equilibrium constants were obtained:

	0°	25°
$10^4 K_1$	10·95	6·89
K_2	2·82	3·12

It was concluded that the possibility of unionized H_2F_2 being present in solutions weaker than $n = 1$ was excluded, and that this indicates either that H_2F_2 is a strong acid or that the addition of a second proton to HF_2^- weakens the hydrogen bond or, possibly, that both propositions are true. This work took no account of the results of Fredenhagen or of Roth, and does not help to clarify the problem of dissociation in hydrofluoric acid.

The thermochemistry of the dissociation processes has been studied by Roth and his co-workers. The heat of neutralization of solutions of strength between N/10 and N/20 was found to be 3·3 kg.-cal. greater than the heat of dissociation of water;[11] as in these solutions there is little dissociation, it was concluded that this difference represents the heat of dissociation of hydrofluoric acid. With this figure, and the values already obtained for the heats of dilution (see page 109) it was possible to calculate the degree of dissociation, and thence the value of K, again assuming only the simple process $HF \rightleftharpoons H^+ + F^-$ to occur. Over a range of dilutions from $v = 1$ to $v = 13$, K was moderately constant, varying between $2{\cdot}15 \times 10^{-4}$ and $2{\cdot}35 \times 10^{-4}$, with an average value of $2{\cdot}2 \times 10^{-4}$, but this does not agree with values of K derived by other means, and in more dilute solutions K was increasing rapidly.

From the temperature variation of the values of K from conductivity measurements, the heat of the overall dissociation was calculated to be 2·8 kg.-cal., which is in good agreement with the figure of 3·3 kg.-cal. obtained from the heat of neutralization; but in view of the lack of any constancy in K, the result was considered uncertain. From the variation with temperature of the values of K from hydrogen ion activities (indicator method), a heat of ionization of 6·2 kg.-cal. was calculated. Again, however, K had been averaged over a wide range, and the authors said the figure had no real significance.

Roth[1] also attempted to calculate K_1 and K_2 in order to obtain heats of reaction for the separate reactions. It has been seen that Hudleston and Davies measured transference numbers, and in calculating the solution composition and K_2, assumed $K_1 = 7{\cdot}4 \times 10^{-4}$. More recently[13] cell e.m.f.s have been measured and a graphical method used to find the most concordant values of K_1 and K_2, from which solution compositions can be calculated. Roth formulated equations by which, from his experimental determinations by the indicator method, he could find the variation of K_1 and K_2 and sought the value of K_1 which gave the least variable K_2. If K_1 was too great, *e.g.* 7×10^{-4} as used by previous authors, $[F^-]$ was greater than $[H^\cdot]$, which is impossible. The more concentrated solutions always gave impossible values for K_2 (either the determination of $[H^\cdot]$ was in error, or, more probably it was considered, the assumption that only two equilibria are involved was incorrect). The calculations were therefore restricted to the more dilute solutions, for which reasonably constant values of K_2 were obtained when the appropriate values of K_1 were used. These were $4{\cdot}0 \times 10^{-4}$ and $2{\cdot}4 \times 10^{-4}$ at 15° and 25° respectively, approximately the values obtained by extrapolating the indicator-method values of K to infinite dilution. Table XXVIII shows the results as given in the original paper, the constancy of K_2 being better than the author expected.

TABLE XXVIII. - COMPOSITION OF HYDROFLUORIC ACID SOLUTIONS (Roth, 1939)

	m	$H^\cdot_\gamma$	F'	HF	HF_2'	K_2
15°	0.1984	0.0191	0.00343	0.1636	0.01567	0.036
	0.1229	0.0120	0.00341	0.1023	0.00859	0.041
	0.0848	0.0092_2	0.00301	0.0694	0.00621	0.034
	0.0518	0.0060_0	0.00284	0.0426	0.00316	0.038
	0.01570	0.0026_3	0.00187	0.0123	0.00076	0.030
	0.01072	0.0020_1	0.00166	0.0084	0.00035	0.040
					Mean:	0.037 ± 0.002
25°	0.1984	0.0168	0.00299	0.1672	0.0138	0.036
	0.1229	0.0106	0.00236	0.1041	0.00824	0.030
	0.0848	0.0074_3	0.00233	0.0723	0.00510	0.033
	0.0518	0.0050_5	0.00208	0.0437	0.00297	0.031
	0.01570	0.0022_2	0.00136	0.0126	0.00086	0.020
	0.01072	0.0016_4	0.00127	0.0087_1	0.00037	0.030
					Mean:	0.030 ± 0.002

K_2 here is $\frac{[F^-][HF]}{[HF_2^-]}$ and is therefore the reciprocal of the K_2 previously used. The values so obtained are then

	15°	25°
$10^4 K_1$	4·0	2·4
K_2	·037	·030
$1/K_2$	27	33

These are very different from the results of Hudleston and Davies. The corresponding heats of reaction are $HF \rightleftharpoons H^+ + F^- + 8{\cdot}5$ kg.-cal., and $HF_2^- \rightleftharpoons HF + F^- + 3{\cdot}6$ kg.-cal.

A fresh attempt was made by Roth to calculate Q_1 from the heat of neutralization[1] and his values for the heat of dilution. The values given in Table XXIX for heats of neutralization of hydrochloric and hydrofluoric acid were determined.

TABLE XXIX. - HEATS OF NEUTRALIZATION, HCl AND HF

	m	*t*°	*Q*
HCl	0·1055	22·73	13·71±0·06
	0·05013	24·18	13·66±0·09
	0·02559	22·99	13·55±0·04
HF	0·1013	19·5	16·86
	0·05213	19·7	16·73
	0·1191	23·36	16·63±0·07
	0·06072	23·55	16·64±0·04

Taking the heat of dissociation of water as 13·55 at 23·36 – 23·55°C. and 13.66 at 19·5 – 19.7°C., the heat of dissociation of hydrofluoric acid was calculated to be:

m	*t*°	*Q*
0·0767	19·6	3·04 kg.-cal.
0·0899	23·45	3·16 kg.-cal.

These values, combined with the heat of dilution and the values of K_1 and K_2 calculated above, gave the values, $Q_1 = 3{\cdot}05$ kg.-cal. and $Q_2 = 5{\cdot}07$ kg.-cal., which show no agreement with the figures obtained above.

Thus, it is seen, Pick's suggestion that the properties of aqueous hydrofluoric acid can be explained by the occurrence of two equilibria and the formation in stronger solutions of the ion HF_2^-, is not supported by the experimental evidence. The conductivity data of various workers are widely at variance and cannot be said to point to the predominance of the simple ionization $HF \rightleftharpoons H^+ + F^-$ in more dilute solutions. Other methods of investigation, determination of transference numbers and hydrogen ion activity, do not give concordant results. Widely differing values of the two equilibrium constants have been calculated, and very discordant heats of reaction obtained by different methods of estimation. Roth, in his later paper, concluded very justly that further and more precise measurements were desirable, and it seems likely that as anhydrous hydrofluoric acid undergoes polymerization beyond the dimeric stage, so in aqueous solution the processes are more complex than was suggested by Pick.

One worker has concluded that the negative ion of hydrofluoric acid is F_2^{--},[15] and the application of a particular cryoscopic method – lowering of the melting point of eutectics – has been held to show that hydrofluoric acid is monomolecular.[16]

Refs p. 119

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HYDROGEN FLUORIDE AS A SOLVENT

Liquid hydrogen fluoride is outstanding as a solvent. It is, indeed, remarkable that any solvent should be able to dissolve, as it does, both inorganic salts such as potassium fluoride and aromatic hydrocarbons such as anthracene. Though a good deal was known about the chemical reactions of the liquid, its behaviour specifically as a solvent had been very little studied until this was examined by Fredenhagen, mainly between 1930 and 1940, and it is to his school that much of the knowledge in this field is due. The study of water-like solvents, which has developed considerably in recent years, has been the subject of a monograph[1], and this particular aspect of the chemistry of hydrogen fluoride has also been reviewed, *e.g.* by Simons[2] and by Sidgwick[3] and others.[4]

That anhydrous hydrofluoric acid has the properties of an ionizing solvent was remarked by Mellor (II, 130) in referring to a very short note by Franklin in 1905. To avoid any confusion in the following section, the term LHF is used throughout in referring to liquid hydrofluoric acid as a solvent: in considering solutions of water, and of compounds which give rise to water on solution in LHF, it would be incorrect to refer to anhydrous hydrogen fluoride; Fredenhagen used the symbols (HF) and (H_2O) when discussing the properties of these compounds as solvents. Mellor (II, 133-4) was in error in stating that the iodides, bromides and chlorides of the alkali and alkaline earth metals are decomposed with liberation of the respective halogen, even though it was possibly the aqueous acid to which he was referring. Neither the aqueous acid nor LHF liberates the halogens from these salts, though LHF certainly liberates the acids and when concentrated hydrogen iodide gas is evolved it can readily give rise to free iodine. Fredenhagen[6] pointed out that there were only two previous workers on LHF solutions: work published by Gore in 1869, although very valuable, contained many incorrect statements; and Franklin, in a footnote to a paper in 1905 where he recorded preliminary results on many solubilities, made the very pertinent observation that LHF, with water and ammonia, was the outstanding electrolytic solvent.

Inorganic salts behave with LHF in a way depending in the first place on the solubility of the fluoride of the metal concerned. Soluble fluorides are not numerous;[5,6,7] they are those of the alkali metals, with solubilities increasing from lithium to cæsium; ammonium fluoride, argentous fluoride and thallous fluoride: of the alkaline earth group, only barium fluoride shows an appreciable solubility, magnesium fluoride being highly insoluble, so that solubility in this group appears to increase as in the previous group. The following quantitative information has been given.

Lithium fluoride, at 18°C. 2·6 g. in 100 cc. of solution:[6] and independently,[8]

temperature, °C.	0	10	20	30	40
moles LiF/mole HF	·043	·037	·045	·042	·044

These latter figures are about twice the former.
The solid phase in equilibrium with these solutions is LiF,HF.[8]

Potassium fluoride, at 0°, 38 g. in 100 cc. of solution:[6] and the following figures are taken from the complete study of the KF–HF system.[9]

temperature, °C.	0	20	40	60
wt.-% KF	25·9	28·5	31·4	35·5

The solid phase in equilibrium with the solution is KF,4HF in each case.

Rubidium fluoride. Quantitative data are not available.[10]

Cæsium fluoride. The following figures are taken from a study of the complete CsF–HF system.[11]

0°		20°		40°		60°	
wt. % CsF	Solid Phase	wt. % CsF	Solid Phase	wt. % CsF	Solid Phase	wt. % CsF	Solid Phase
65·0	CsF,3HF	67·8	CsF,3HF	77·3	CsF,2HF	83·5	CsF,HF
		75·2	CsF,3HF	80·8	CsF,2HF		
		75·7	CsF,2HF	81·2	CsF,HF		

Silver fluoride, at -15°C. 33 g. in 100 cc. of solution.[6] A part of the *ammonium fluoride-hydrogen fluoride* system has been studied.[12]

The fluorides of *aluminium, zinc, iron* (ferric), *lead* (plumbous), *copper* (cupric) and *mercury* (mercuric) are said to show no appreciable solubility,[6] and *calcium, zinc,* and *magnesium* fluorides show less than 0·01% solubility at 0°C.[8] *Chromium fluoride* is also said to be soluble.[8]

The behaviour of any given salt with LHF depends both on the solubility of the fluoride of the metal, and on the solubility of the acid corresponding to the anion of the salt. Hydracids are but slightly soluble in LHF, whilst oxyacids are in general soluble, although further decomposition or other reactions may occur. Hydrogen chloride, bromide, iodide, cyanide, azide[6,13] and sulphide[14] are but very slightly soluble, (an earlier statement is that hydrogen sulphide is soluble);[6] carbonic acid,[5,15] and silicon tetrafluoride[6] are insoluble. The corresponding alkali metal salts dissolve as fluorides, with rapid liberation of these acids. In other cases reaction may occur in spite of the insolubility of the fluoride. Thus, aluminium, ferrous, manganous and cerous chlorides react, whilst the following are said to be unchanged[6] – $ZnCl_2$, $SnCl_2$, $NiCl_2$, $CdCl_2$, $CuCl_2$, CuCl, $HgCl_2$, HgI_2, AgCl, AgBr, AgI. The opinion has been expressed that all chlorides will gradually decompose with LHF,[15] the rate depending on the solubility of the fluoride, but the salts of silver and thallium are exceptions to this as they can be precipitated[15] (see below).

Ruff has also stated[16] that most chlorides, bromides and iodides react with pure hydrogen fluoride according to the equation

$$n\mathrm{HF} + \mathrm{MCl}_n \rightleftharpoons \mathrm{MF}_n + n\mathrm{HCl},$$

and instances as fluorides made in this way, TiF_4, ZrF_4, VF_4, VOF_3, VF_3, NbF_5, TaF_5, SnF_4, SbF_5. From his account of the preparation of these compounds, it is not clear whether they may not be first obtained in solution in LHF. A later paper suggests that in the case of antimony pentafluoride there is complete miscibility.[17]

The typical reaction of carbonates has been shown to occur with those of lead, zinc, and calcium[15] and potassium fluosilicate has been found to react with violent evolution of silicon tetrafluoride.[6]

Whilst the cyanides and azides of the alkali metals generally behave like the halides, the corresponding acids being liberated by LHF, there are some exceptions. Mercuric cyanide is very soluble,[6] silver cyanide is slightly soluble, argentous azide and mercuric azide are very soluble and thallous azide also is soluble,[13] all giving solutions from thich the salts can be obtained unchanged on evaporating the solvent, thus emphasising the covalent character of these particular compounds. Fluoborates also react, as boron trifluoride is only slightly soluble.[2] The field of the complex fluorides has, however, been very little explored. Fluorocolumbates are formed by crystallization of mixtures of LHF solutions of sodium and columbium fluorides[18] and alkali metal hexafluorophosphates are precipitated by reaction of the chlorides with phosphorus pentachloride in LHF.[19] In a recent study, Woolf obtained potassium fluoborate by passing boron trifluoride into an LHF solution of potassium fluoride at -78°.[20] In the same work, hydrogen fluoride was condensed at -78° on to mixtures of potassium bifluoride and fluorosulphonate, and of potassium bifluoride and antimony pentafluoride, and on evaporating the hydrogen fluoride, the pure salts KSO_3F and $KSbF_6$ were obtained. Mixtures of barium chloride and antimony pentachloride, on the other hand, gave a product containing chlorine. The halogen fluorides are completely miscible in all proportions with anhydrous hydrofluoric acid, and solutions can thus be obtained of chlorine trifluoride, chlorine monofluoride, bromine tri- and pentafluoride and iodine penta- and heptafluoride;[21] a boiling point curve is given for HF ClF_3. Woolf[20] found, however, that on evaporating an LHF solution of equimolecular amounts of potassium bifluoride and iodine pentafluoride a fuming white solid retaining some hydrogen fluoride was obtained; chlorine trifluoride similarly treated gave no reaction product, the residue on evaporation being free from chlorine. On evaporating an iodine pentafluoride solution, no additive compound containing hydrogen fluoride was obtained. It was concluded that the preparation of complex fluorides in LHF has limitations attributable to the solubilities of many fluorides and to the retention of solvent owing to solvolytic or co-ordination phenomena.[20]

Among oxyacids, the appropriate nitrates, sulphates, perchlorates,[6] iodates and periodates,[15] are soluble; chlorates dissolve with decomposition to give a solution containing chlorine dioxide,[6] bromates decompose with evolution of oxygen to give a solution containing bromine,[15] nitrites give nitrous gases.[15] Chromates and permanganates dissolve, but give greenish or reddish vapours which can be shown to contain heptavalent manganese and sexavalent chromium respectively, and are suspected to be oxyfluorides.[15] Persulphates dissolve, but readily evolve oxygen, *e.g.* on addition of potassium nitrate or thallium nitrate.[15] Hydroxides dissolve or react, and many oxides react, calcium oxide with incandescence; MgO, SrO, BaO, PbO also react strongly, Al_2O_3, CuO react slowly while HgO, PbO_2, MnO_2, SnO_2, Cr_2O_3, WO_3 and Mn_2O_3 are unchanged. Silver oxide dissolves rapidly and barium peroxide evolves oxygen.[6]

All these solutions show high electrical conductivity,[5,6,7,22] and, as in aqueous solutions, the equivalent conductivity increases on dilution; with certain simple compounds, such as water, potassium fluoride and silver fluoride, the conductivity at infinite dilution, Λ_∞, approaches 260 at −15°C. The degree of dissociation at intermediate dilutions is calculated from the conductivity and in the case of the three compounds named 0·5N.solutions show 46%, 65% and 66% dissociation, respectively. For the fluorides, the dissociation is expressed by $KF \rightleftharpoons K^+ + F^-$, but for water it is $H_2O + HF \rightarrow H_3O^+ + F^-$ and not, as might be expected, into hydrogen and hydroxyl ions. Thus the conductivity of a solution containing both potassium fluoride and water is equal to the sum of the conductivities of separate solutions of each of the same concentration. In the case of solutions of oxysalts, such as potassium nitrate, however, much higher conductivities are obtained, and the explanation which is advanced, supported by determinations of boiling point elevation,[22] is that the dissociation occurring is $KNO_3 + 2HF \rightarrow K^+ + H_2NO_3^+ + 2F^-$, so that four ions are produced from one molecule of potassium nitrate. A similar phenomenon occurs with potassium acetate, and in this case it may be shown that the conductivity is equal to the sum of the conductivities of separate solutions of potassium fluoride and acetic acid of equivalent concentration.

The explanation advanced by Fredenhagen to account for these phenomena is that hydrogen fluoride forms addition complexes with the oxygen compounds, which then ionize with the formation of a fluoride ion and a positive complex ion. With water, for example, the process would be

$$H_2O + HF \rightarrow H_3OF \rightarrow \left[\begin{smallmatrix}H\\H\end{smallmatrix}\!>O-H\right]^+ + F^-.$$

In the light of the foregoing discussion on the association of hydrofluoric acid and its ionization in aqueous solution, this is perhaps an over-simplified view. The molecular species present in the liquid are the dimer (H_2F_2) and higher polymers, and it is probable, as pointed out by Sidgwick,[3] that the negative ion is not the simple ion $[F]^-$ but the bifluoride ion $[HF_2]^-$, although for simplicity we may usually write $[F]^-$ just as in aqueous solutions we usually write $[H]^+$ for $[H_3O]^+$. Rather than relating ionization in LHF to the preliminary formation of hydrogen fluoride addition complexes with receptor molecules, we should, more probably, ascribe it directly to a proton donor-acceptor mechanism. It may be suggested that not the dimer only but all the polymers in the liquid readily donate a proton, and it is indeed worth examining the possibility that not only the ion $[HF_2]^-$ but also $[H_2F_3]^-$ and even higher species may exist in aqueous solutions. The behaviour of water as a proton acceptor conforms with its behaviour in aqueous solutions, but there appears immediately a strong contrast between the processes of ionization in aqueous and in LHF solutions. In the former the solvent will act as a proton acceptor, and proton donors give strongly ionized solutions, the proton demand of the solvent being sufficient to 'de-ionize' the cation of dissolved salts of weak electrolytes by the reaction $MX \rightarrow M^+ + X^-$: $M^+ + 2H_2O \rightarrow MOH + [H_3O]^+$. In LHF, on the other hand, the solvent acts as a proton donor, and proton acceptors give strongly ionized solutions (as is richly illustrated by the behaviour of organic solutes; see below). The ability of the solvent to donate protons is so great as to de-ionize anions of dissolved salts to a much greater extent than in the comparable process in water, and even to force them to behave as proton acceptors. Combined oxygen can be regarded in general as a proton acceptor, or, in a modified form, as giving rise to association by hydrogen bonding, *e.g.* in carboxylic acids; and the formation of complexes of hydrogen fluoride with perchloric acid and other oxyacids has been observed in other work.[23] The generalized theory of acids and bases associated with the names of J.N. Brønsted and T.M. Lowry accords with these views. Solvents fall into three categories: proton acceptors, basic or protophilic; proton donors, acidic or protogenic; and solvents that are neither donors nor acceptors, aprotic. LHF is thus a powerfully protogenic solvent and in it acids, such as nitric acid, are bases; (for a general account of this matter see, *e.g.*[24]) These properties have also been discussed from the point of view of hydrogen bonding.[25]

Fredenhagen was at first inclined to suggest that the fluoride ion was the only anion which could exist in LHF,[22] but more detailed studies have shown that this is by no means the case.[15] He has found that his earlier observations exaggerated the insolubility of halogen hydracids, and that these gases, bubbled through LHF solutions of silver and thallium salts, will give precipitates of the corresponding halides. Precipitation reactions also occur with solutions of perchlorates, periodates, and sulphates. The perchlorate ion is outstanding in its ability to co-exist in LHF with the fluoride ion; the perchlorate ion indeed rivals the fluoride ion as a proton donor, as fits the observation that perchloric acid is the strongest acid in the aqueous system.[24]

For the study of LHF solutions, supplies of hydrofluoric acid of high purity were required, and its suitability for conductivity studies was shown by its low conductivity, indicating a low water content. The steps taken to obtain these supplies have been described above (see page 88), and the work on conductivity measurements has also been referred to. In addition, ebulliometric methods have been developed for use in LHF.[26,27,28] It was a matter of some difficulty to find non-ionizing solutes for determining the molecular elevation of the boiling point, but by using benzoyl fluoride, benzonitrile, or trichloroacetic acid a figure of 1·90° was found, in good agreement with that theoretically derived after allowing for the degree of association (see page 92). Determinations of b.p. elevation give a measure of the total number of foreign particles in the LHF solutions, and not only of the ionized particles indicated by the conductivity determinations. They confirm the increased number of particles in the case of salts such as potassium nitrate and acetate, and help to clarify the behaviour of sulphate solutions. The conductivity of an LHF-sulphuric acid solution increases, over a period of 30 minutes after its first production, to several times its original value:[6,15] this is attributed to the formation of water by the relatively slow reaction $H_2SO_4 + HF \rightarrow HSO_3F + H_2O$, the final conductivity of the solution being equal to that of the equivalent LHF solution of water. Ebulliometric measurements show also the presence of other particles which do not contribute to the conductivity, presumably fluorosulphonic acid molecules. With potassium sulphate, the reaction is $K_2SO_4 + 2HF \rightarrow KSO_3F + H_2O + KF$, and the conductivity is principally attributable to the water and potassium fluoride, with a relatively small contribution from the potassium fluorosulphonate. Both freshly prepared and 'aged' LHF solutions of sulphuric acid and of sodium sulphate (which is very soluble) give a precipitate of silver sulphate with strong LHF solutions of silver salts, so that some sulphate ion is, presumably, always present.[15]

The chemistry of these solutions has obviously been very little explored, and there is room for much further work, both in refined measurement and in further study of detail. Thus Fredenhagen had satisfied himself by a simple test that the solubility of hydrogen chloride was very low, but was later able to show that he had underestimated this, and where his error lay. Again, whilst at ordinary temperatures (in the neighbourhood of 0°C.) chlorates and bromates dissolve with decomposition, this is not evident at lower temperatures.[15] It may be expected that such salts as permanganates and chromates also may give useful solutions at lower temperatures, although the tendency to form oxyfluorides, noted here as well as in the case of sulphuric acid, will probably occur in many other cases to a greater or lesser extent. Further study in this field offers considerable opportunities: the choice of metal cations available is limited by the insolubility of the majority of metal fluorides, and the range of anions studied is not, so far, very extensive, but there is a very great choice of complex cations, organic proton acceptors, offering a wide field for further exploration.

As water, behaving as a proton acceptor, gives a highly conductive LHF solution, it is not surprising that the alcohols show the same effect. Methyl alcohol was found to give a solution having high conductivity,[5] and other alcohols – ethyl, *n*-propyl, *n*-amyl – behaved similarly, the values of the conductivities at infinite dilution approaching 260.[6] It has been concluded that this high value is due principally to the great mobility of the fluoride ion in this solvent,[22] and the conductivities of the four alcohols in 0·5 N. solution indicates dissociations of 54%, 64%, 59% and 56% respectively.[6] It is, however, hardly correct to apply the term dissociation to what is occurring here. From the conductivities, the degree to which the solute molecules have acquired polar character is calculated, but this acquisition is by association (addition of a proton) and not dissociation.

Not only alcohols but a wide range of types of organic compounds are soluble in LHF, and the solutions show electrical conductivity to a varying extent. Measurements of conductivity and boiling point elevation have been made on many solutions by Fredenhagen's school and particularly by Klatt, one of his pupils. With the aliphatic monohydric alcohols[6,29] the rise in b.p. suggests that some alkyl fluoride is formed though quantitative proof of this was not possible; and ethyl fluoride in LHF, with the equivalent amount of water, was found to produce alcohol, but again it could not be decided whether the reaction was complete. There is in all cases the possibility of an equilibrium, $ROH + HF \rightleftharpoons RF + H_2O$, when the water produced will act as a proton acceptor: the conductivity of the solution will give no guidance as to the extent of reaction, but the rise in b.p. will show a higher proportion of foreign particles. Alcohols with double bonds in the molecule, *e.g.* benzyl alcohol, are often, though not always, polymerized by hydrogen fluoride;[29] if the double bond is close to the proton-accepting oxygen, there is no polymerization and no addition of hydrogen fluoride across the double bond. Thus allyl alcohol gives a conducting solution which, however, unlike the colourless solutions of saturated alcohols, is deep red in colour. Polyhydric alcohols also show anomalies: ethylene glycol gives a solution of much lower conductivity and b.p. rise than might be expected; glycerol shows a very high conductivity, whereas that of mannitol is very low, whence it appears that the spatial relation of the hydroxyl groups is the controlling factor. It is said that the rise in b.p. is approximately doubled (as against that for a single hydroxyl group) if there are hydroxyl groups in the 1:3 position and having the same spatial direction.[29] With phenols, proton demand is diminished; they tend to form coloured solutions with no fluoride formation. The fact that conductivity is enhanced with resorcinol and pyrogallol but is almost zero with pyrocatechol and hydroquinone is explained by the 1:3 rule given above. With the naphthols the α-compound shows higher equivalent conductivity and greater b.p. elevation than the β-, and this may be related to the proton demand of the aromatic nucleus itself (see below). The proton demand of phenolic hydroxyl is reduced by negative substituents in the ring, and this affects the solubility also. Thus while phenol is soluble, nitrophenol is only moderately so, and picric acid is practically insoluble; the chloro- and bromo- phenols show the same effect.

Carboxylic acids behave very much as the alcohols, and the following 'degrees of dissociation' of 0.5 N.solutions have been given[30] (all as percentages): formic, 10: acetic, 56: benzoic, 47: salicylic, 69: cinnamic, 63: *m*-nitrobenzoic, 7: mono-, di- and trichloroacetic, 2, nil and 3 respectively: oxalic, 17: malonic, 42: succinic, 85: glutaric, nil: adipic, nil. With many of these acids, however, the rise in b.p. shows a greater number of particles than does the conductivity, and it appears that the tendency to fluoride formation is greater with acids than with alcohols. In the case of benzoic acid the presence of benzoyl fluoride may be demonstrated by extracting the LHF solution with ligroin, in which the acid is insoluble, whilst the partition coefficient of the fluoride between this solvent and LHF is about unity, though on attempting to isolate the fluoride by evaporating the solvent the reaction reverses. The tendency to form the acid fluoride varies with the acid, being much less with acetic, cinnamic and salicylic acids. It is, of course, possible that the oxygen in the acid fluoride may still show some proton demand. An attempt was made to cause the water (which would be formed along with the fluorides) to react with fluorine in presence of silver fluoride and other salts, but although preliminary experiments were said to have shown interesting results no further work has been reported.[30] Acid anhydrides in some cases show high conductivities (e.g. benzoic anhydride), in others none. Among the many organic compounds studied, maleic anhydride was almost the only one which was readily soluble in LHF and yet gave the calculated rise in b.p.[30]

The influence of the structure on the proton demand, as indicated by the figures given above, is interesting, especially in the chloroacetic acid series where the proton demand diminishes with successive chlorine substitutions. In the aqueous solutions, the strength of these acids increases from acetic to trichloroacetic, as the ability to donate protons increases in this order. Obviously these two characteristics are closely, though inversely, related, and this consideration brings out clearly the contrast between water and LHF; in water, the solvent acts as a proton acceptor and compounds that are poor proton donors do not show high conductivity. For that very reason these same compounds in LHF, where the solvent acts as proton donor and the solute as proton acceptor, show high conductivities. Whilst this is well exemplified in the acetic acid series and is also borne out by the halogen hydracids which show no proton demand in LHF, it is not well exemplified by the inorganic oxy-acids, such as sulphuric, nitric, and perchloric acids, and it is not clear why trichloroacetic acid and, say, perchloric acid should behave so differently.

Aromatic hydrocarbons show appreciable solubility in LHF, and give coloured solutions, as shown in Table XXX.[31]

TABLE XXX.- WEIGHT PERCENT OF HYDROCARBONS SOLUBLE IN LHF.

Temp °C.	Benzene	Toluene	Anthracene	*m*-Xylene	*o*-Xylene	Tetralin
+15	3·11	2·43	–	–	–	–
10	2·82	2·05	3·43	–	–	–
5	2·54	1·80	3·27	1·28	1·12	0·27
0	2·26	1·54	3·11	1·17	1·01	0·23
– 5	2·05	1·34	2·96	1·08	0·94	0·21
–10	1·88	1·25	2·88	1·01	0·87	0·19
–15	1·67	1·12	2·77	0·95	0·85	0·15
–20	1·56	1·02	–	–	–	–
Colour	none	red-brown	dark olive	–	–	red-brown

More remarkable still, the solutions show pronounced conductivity, of a similar order to that of other LHF solutions, a 0·01 N. solution of anthracene having an equivalent conductivity (-15°C.) of 300. The concept of proton demand discussed above, when applied to the conductive behaviour of aromatic hydrocarbons, may be related to the concept of carbonium ion formation and the basicity of olefinic hydrocarbons which has been found of value in explaining acid-catalyzed hydrocarbon reactions,[32] and the solubility of aromatic hydrocarbons in LHF has already been advanced as evidence of their possessing proton affinity.[33] It is found, moreover, that certain soluble salts cause an increase in solubility, and colour changes in the solutions. Mercuric cyanide and azide, silver azide and fluoride, and thallous fluoride have this effect. Although the salts themselves give colourless solutions, the reddish brown toluene solution becomes colourless on adding silver azide, pale yellow with mercuric azide, and a stronger red with the other salts. Whilst phenanthrene dissolves only very slightly in LHF alone, the solubility is increased by these salts and a bluish-green solution is obtained. This may be used as a test for traces of silver in LHF, phenanthrene crystals becoming coloured if silver is present. The hydrocarbons cause an increase in the solubility of the salts also; and the suggestion is made that the solutions show a ratio of four molecules of hydrocarbon to one of salt (the thallous salt being different, probably 2:1). Saturated hydrocarbons (methane, pentane, *cyclo*hexane, methyl*cyclo*hexane) have been said to show no appreciable solubility and no metal salt influence, but later work requires some modification of this statement. In connexion with the development of hydrogen fluoride catalysis in the petroleum industry, (see pages 135,142) there is much interest in these solubility relations, and in a report giving the data,[34] solubilities in LHF, as weight percentages, are given by: *iso*butane, $\log_{10} W = -\frac{630\cdot3}{T} + 2\cdot69027$; *n*-butane, $\log_{10} W = -\frac{569\cdot0}{T} + 2\cdot32359$; propane, $\log_{10} W = -\frac{605\cdot2}{T} + 2\cdot74152$; the respective solubilities at 0°C. being 2·41, 1·74, 3·35%. Data are also given for the hydrogen fluoride content of the hydrocarbon phase, and it is found that higher hydrocarbons, 'alkylates' (*iso*paraffins approximately of the heptane and octane series), reduce the solubility considerably, as does water.

Unsaturated hydrocarbons, in their behaviour with LHF, fall into three classes: (1) those showing some solubility, influenced by metal salts; (2) those undergoing polymerization, *e.g.*, amylene, butadiene, indene; (3) those remaining insoluble, *e g.*, diphenyl. Figures have been given for the solubility of hydrofluoric acid in benzene and octane.[35] Among other classes of compounds, ketones give highly conductive and strongly coloured solutions;[28,36] with acetone and acetophenone, there was no indication of condensation reactions and aldehydes behaved similarly.[36] Among nitrogen compounds,[14] salt formation occurs in many cases and the fluorides (or hydrofluorides) are soluble; aniline, napthylamine, urea etc. behave in this way. Heterocyclic nitrogen compounds, pyridine and quinoline for example, may also behave similarly, but in other cases, as with pyrrole, polymerization rapidly occurs. Azo compounds also form salts, *e.g.* azobenzene forms salts with 1HF and 2HF, and these compounds give coloured solutions of high conductivity; p-aminoazobenzene gives a perfectly clear but dark red, almost black, solution, showing a considerable rise in b.p., and other azo-compounds give other colours. Diazo compounds also give strongly coloured solutions, in which the colour is not due to any dyestuff-forming coupling and there is no rearrangement or resinification. Diazoaminobenzene dissolves in LHF to a dark red to violet solution, and at higher concentrations and temperatures the hydrogen fluoride vapour carries with it an orange-yellow to red vapour from which fluorobenzene can be obtained while aniline may be obtained from the residual solution. At low temperatures benzenediazonium fluoride can be obtained as fairly stable white crystals The effect of the nitro-group on the solubility of the phenols has already been noticed, and the same effect is seen with nitrobenzoic acid, which shows a much lower conductivity than benzoic acid. In these cases the nitro-group has the same effect as substituted chlorine or bromine. On the other hand the nitro-group can also increase the proton demand of inert compounds, so that the solubility of nitrobenzene, and its conductivity, are very much greater than those of benzene itself. No such effect is shown by chlorine or bromine, monochlorobenzene having a low solubility and monobromobenzene being almost insoluble. Of sulphur compounds, mercaptans behave like alcohols, ethyl mercaptan and diethyl sulphide dissolving readily and showing good conductivity without any tendency to split off hydrogen sulphide (which has a low solubility in LHF). Thiourea dissolves readily and generally behaves like urea. Thioacetic acid, $CH_3.COSH$, however, readily loses hydrogen sulphide and gives the acid fluoride. Thiophene reacts to give a red solid which was not further investigated, and thionaphthene slowly dissolves to a clear red-brown solution which in a few minutes goes cloudy owing to polymerization. Sulphonic acids behave like sulphuric acid, and give the sulphonyl fluorides.[14] There has been little direct practical application of this work in chemistry, although it may be assumed that in the very considerable development of hydrofluoric acid catalysis in the petroleum industry solvent action must play a prominent part. It has also been suggested that unusual results are obtained in an LHF medium in oxidizing organic compounds with elementary oxygen under pressure.[37]

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THE CHEMICAL PROPERTIES OF HYDROFLUORIC ACID

Hydrofluoric acid shows a very general tendency, already considered (see page 122), to react with other compounds and form fluorides. The opposite tendency, for hydrogen fluoride to be liberated, is less frequently observed, but quite often potential reactions may be inhibited by limitations of a physical rather than of a chemical nature. Thus, in considering the solvent properties of hydrofluoric acid (see page 120), it is shown that the insolubility of the fluoride produced may sometimes limit the reaction of the compound. Thus calcium oxide reacts very violently with the liquid, though calcium fluoride is insoluble; but alumina does not react, and has been found valuable as a material resistant to fluorine and hydrofluoric acid. This inhibiting action of a fluoride film occurs also with metals, most of which will reduce hydrogen fluoride (see pages 62 and 143). The equilibrium of many fluorides with steam, studied in the work of Domange (see page 73), is found to be in favour of hydrogen fluoride reacting with the oxide. Fredenhagen considered that almost all chlorides will react, although with some the reaction is extremely slow; but hydrogen chloride will precipitate silver and thallium chlorides from LHF solutions (liquid hydrogen fluoride - see page 121).

Fredenhagen, as seen on page 120, considered only ionic chlorides, and only their reactions with liquid hydrofluoric acid, but the less ionic chlorides behave in a similar manner, and may equally show the reaction with vapour. Thus, sometime prior to Fredenhagen's work, Ruff had summarized his wide experience in preparing fluorides in the statement quoted on page 121.

Sometimes reactions of this character, as we shall see, produce mixed halides. The more covalent oxides, and acidic oxides also, tend to form oxyfluorides, as is seen with sulphuric acid in LHF: covalent oxyfluorides of this character tend to be formed also when the corresponding oxychlorides react with hydrofluoric acid.

Most of the published work on halogen interchange relates to chlorides; there is little concerning bromides and iodides. The general case of fluoride-chloride interchange is conveyed[1] by Table XXXI, where values are given for the difference in free energy between the chloride and the fluoride per g. atom of halogen.

TABLE XXXI. - FREE ENERGY OF CHLORINE-FLUORINE EXCHANGE AT 25°C. (ALL SOLIDS EXCEPT WHERE OTHERWISE INDICATED). (SEE ALSO TABLE XXXIa)

System	$\Delta F^\circ_{MCl} - \Delta F^\circ_{MF}$ g.-cal.	System	$\Delta F^\circ_{MCl} - \Delta F^\circ_{MF}$ g.-cal.
$AgF - AgCl$	17,800	$\frac{1}{2}(NiF_2 - NiCl_2)$	40,300
$CsF - CsCl$	24,500	$\frac{1}{2}(BaF_2 - BaCl_2)$	40,300
$RbF - RbCl$	27,300	$\frac{1}{3}(SbF_3 - SbCl_3)$	40,500
$KF - KCL$	29,100	$HF_{(g. ideal)} - HCL_{(g)}$	40,900
$\frac{1}{4}(CF_{4(g)} - CCl_{4(g)})$	33,400	$\frac{1}{2}(SrF_2 - SrCl_2)$	44,300
$\frac{1}{2}(CdF_2 - CdCl_2)$	34,100	$LiF - LiCl$	46,300
$\frac{1}{2}(PbF_2 - PbCl_2)$	34,700	$\frac{1}{2}(CaF_2 - CaCl_2)$	48,300
$NH_4F - NH_4Cl$	34,700	$\frac{1}{3}(AlF_3 - AlCl_3)$	52,600
$\frac{1}{2}(ZnF_2 - ZnCl_2)$	36,200	$\frac{1}{4}(SiF_4 - SiCl_4)$	53,900
$NaF - NaCl$	36,400	$\frac{1}{2}(MgF_2 - MgCl_2)$	53,900
$\frac{1}{2}(CuF_2 - CuCl_2)$	38,300	$\frac{1}{3}(BF_3 - BCl_3)$	55,700

Some of these data are said to be not highly accurate. The difference is not very great in favour of silver fluoride, very much greater for hydrogen fluoride and greater still for boron trifluoride. The reactions with hydrofluoric acid of the chlorides above hydrogen chloride in this table, may be expected to proceed only partially: but naturally, from energy considerations, they will go more readily with liquid than the Table shows, since this refers to the unassociated vapours.

In a later paper,[2] the equilibrium HF + NaCl $\rightleftharpoons$ HCl + NaF was studied, and the results are given in Table XXXII.

TABLE XXXII. - EQUILIBRIUM IN THE SYSTEM (HF - NaCl - HCl - NaF.)

t, °C.	523	526	550	561	589	595	669
K	0.029	0.0292	0.0325	0.0342	0.0372	0.0386	0.0500
ΔF°g.-cal.	5600	5610	5580	5570	5620	5620	5610

The equilibrium was approached from either side in alternate experiments; it is clear that this makes little difference, and that the equilibrium lies to the left hand side, as would be expected from the data of Table XXXI.

At room temperature it was found that a polyhydrofluoride was formed, in conformity with the results of Fredenhagen and others on the reactions of alkali chlorides with pure liquid hydrofluoric acid and also with the prediction made above; but at 200°C. there was no reaction. In the same paper, the results of certain other equilibrium studies were given, as summarized in Table XXXIII.

TABLE XXXIII. - EQUILIBRIUM OF VARIOUS CHLORIDES WITH HF

System	Temp. °C.	*K*	ΔF° g.-cal.
$BaCl_2$ + 2HF	204	0.00193	5920
	760	0.0546	5970
$NiCl_2$ + 2HF	204	0.2262	1410
	560	0.4288	1400
$PbCl_2$ + HF	280	0.2125	1700
	395	0.2682	1750

These results do not conform very precisely with the data of Table XXXI, which lead to the expectation that the barium and nickel salts would be much more alike in behaviour, and more nearly like nickel in the above table. It may be noted that lead chloride only gave the chlorofluoride and would not readily go to the fluoride. As a result of this work, a corrected list of free energies was given for the cases studied, Table XXXIa.

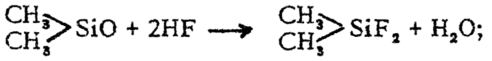
TABLE XXXIa. - CORRECTED FREE ENERGIES OF CHLORINE-FLUORINE EXCHANGE

System	$\Delta F^\circ_{MCl} - \Delta F^\circ_{MF}$ g.-cal.
$\frac{1}{2}(BaF_2 - BaCl_2)$	36,200
NaF - NaCl	36,900
PbClF - $PbCl_2$	40,600
$\frac{1}{2}(NiF_2 - NiCl_2)$	40,800
$HF_{(g)} - HCl_{(g)}$	42,200

The interaction of beryllium chloride with hydrofluoric acid in aqueous solution has been observed.[3] One case of fluoride exchange which has received a good deal of attention is that of organic halides. Organic halogen compounds undergo reaction with hydrofluoric acid, and with a great variety of fluorides, with varying facility. The subject in general is one for treatises on organic chemistry[4] but the simple aspect of exchange with hydrogen fluoride is of interest here. With some reactive -CCl_3 groups, complete conversion to -CF_3 takes place on heating with anhydrous hydrofluoric acid under pressure, as in the case of benzotrifluoride, but this is not so with carbon tetrachloride. In the vapour phase, reaction proceeds readily on heating to give monofluorotrichloromethane, $CFCl_3$, but above 450°C. more of the difluoro-compound, CF_2Cl_2, is formed; the reaction is catalyzed by ferric chloride on charcoal.[5] The reaction may be carried out at lower temperatures under high pressure, *e.g.* at 230°C. and 1000 lb./sq.in.[6] Using hydrofluoric acid alone, the replacement of further chlorine atoms becomes increasingly difficult but the use of antimony trifluoride as catalyst greatly facilitates the reaction, especially if some of the antimony has been converted to the pentavalent state by chlorination. It is also claimed that the partially fluorinated products can be converted into carbon tetrafluoride by reaction with hydrogen fluoride over a ferric or chromic fluoride catalyst at elevated temperatures.[7] A mixture of carbon disulphide with hydrogen fluoride and chlorine passed over a copper chloride catalyst at 200 – 400°C. yields difluorodichloromethane: monofluorotrichloromethane is obtained from the same reactants over a chromic fluoride catalyst at 450 – 500°C., and the catalytic effect of other halides is referred to.[8] These fluorochloro derivatives of methane (and of other hydrocarbons) are well known as refrigerants under the trade mark 'Freon'. Similarly phosgene gives carbonyl chlorofluoride[9] or fluorophosgene[10] according to the conditions of reaction.

Turning to other elements of Group IV, it appears that at relatively low temperatures silicon tetrachloride and hydrogen fluoride co-exist, and the compounds $HF,SiCl_4$ and $4HF,SiCl_4$ have been reported;[11] no indication is given of any reaction. In the case of titanium tetrachloride, on the other hand, Ruff[12] describes the very vigorous reaction that occurs on adding it dropwise to anhydrous hydrofluoric acid, with evolution of clouds of hydrochloric acid. It is recommended that only half the theoretical amount of titanium tetrachloride should be added, while cooling in ice and salt: afterwards, the mixture is allowed to warm up slowly over several hours and then the excess of hydrogen fluoride is driven off on an oil bath which is finally heated to 200°C. to give titanium tetrafluoride. Zirconium tetrachloride reacts in a similar manner,[12] and the reactions of thorium tetrachloride and tetrabromide to give the fluoride have also been described.[13] Stannic chloride also reacts readily, but a double salt $SnCl_4,SnF_4$ is obtained[12] which decomposes on heating to 130 – 220° when stannic chloride distils off and leaves the fluoride (b.p. 705°). In Group V, little is known of the reactions of nitrogen trichloride and the phosphorus chlorides with hydrofluoric acid, though a recent paper refers to the formation of phosphoryl fluoride from the chloride,[14] and the production of hexafluorophosphates by the reaction with phosphorus pentachloride has been described.[15] Vanadium tetrachloride and the pentachlorides of niobium and tantalum react readily, and it is recommended that the reaction mixture should be refluxed for ½ – 2 hours, until no more hydrochloric acid is evolved.[12] Ruff also described how unreadily vanadium trichloride reacts, in comparison with the tetrachloride; the latter reacts vigorously with liquid anhydrous hydrofluoric acid in the cold, and on driving off excess hydrofluoric acid at 50° pure vanadium tetrafluoride is obtained. The trichloride, on the other hand, shows little reaction below 100° and must be heated for 6 – 8 hours at a dull red heat in a stream of hydrogen fluoride vapour, to obtain pure vanadium trifluoride. Vanadium oxytrichloride behaves like the tetrachloride and readily gives VOF_3, whilst the oxydibromide behaves like the trichloride and gives VOF_3 only with difficulty.[16] The observations regarding the reaction of the trichloride have been confirmed more recently, a temperature of 600°C. being required; whilst the dichloride reacted with even greater difficulty, and at 700°, in a stream of hydrogen fluoride, only the trifluoride was obtained.[17] Antimony pentachloride, Ruff reported,[12] reacts readily and this method has been the subject of a patent[18] for making the pentafluoride. In Group VI nothing is known about the reaction of the chlorine oxides or the sulphur chlorides with hydrofluoric acid, but thionyl chloride and sulphuryl chloride react to give the corresponding fluorides.[14] In the general paper considered above, Woyski[1] reported obtaining the mixed chlorofluoride, SO_2ClF, from sulphuryl chloride and potassium bifluoride or ammonium fluoride (but not magnesium, calcium, barium or lithium fluoride). Moreover, either sulphuryl chloride or the chlorofluoride (or indeed an equimolecular mixture of sulphur dioxide and chlorine) with potassium fluoride at 400°C. quantitatively afforded sulphuryl fluoride, SO_2F_2, whereas in the presence of other fluorides only partial reaction was observed. The limiting free energy difference (Table XXXI) is therefore considered to be 29,000 g.-cal. Molybdenum pentachloride gave only traces of a readily volatile molybdenum halide when heated with hydrofluoric acid, but the oxy compounds $MoOCl_4$ and MoO_2Cl_2 readily gave the corresponding fluorides.[19] Molybdenum tribromide slowly yielded the trifluoride when heated for several hours at 300 – 600° in hydrogen fluoride, whilst the dichloride and the dibromide under these conditions were practically unattacked, and only at 730°C did a slow reaction occur [17] Tungsten hexachloride readily gave WF_6, and $WOCl_4$ also reacted readily, but the formation of WO_2F_2 was in doubt.[20] The reaction of uranium pentachloride and hexachloride, to give the fluorides, has been the subject of a patent.[21] Information is lacking on the reaction of the selenium and tellurium halides, though the formation of the oxyfluorides has been observed,[14] and nothing is known of the reactions of the higher halides of Group VII.

The reaction of oxides with hydrofluoric acid has been mentioned above. For the aqueous acid, it is controlled by the well known factors governing reactions with acids, but the reaction of the anhydrous acid with oxides differs from that with halides, because water and hydrofluoric acid are completely miscible whereas the hydrogen halides are almost insoluble in LHF. The reaction of acidic oxides with hydrogen fluoride may, however, be very different from that with other hydrogen halides, because of the much greater stability of certain fluorides in water compared with the other halides. Thus boric acid in aqueous solutions readily forms hydrofluoboric with hydrofluoric acid; the rate of this reaction has been studied and a reaction mechanism proposed.[22] The silicon system is very similar. It has, however, been seen above that in the absence of moisture silica is not attacked by hydrofluoric acid, so that water, besides being a product of the reaction, must play a fundamental part in the mechanism. It is interesting to note that silicones react rapidly with anhydrous liquid hydrofluoric acid to give the corresponding fluorosilanes:



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>SiO + 2HF \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>SiF_2 + H_2O;$$

the reaction being catalyzed by copper sulphate.[23] Phosphorus pentoxide reacts with strong (or anhydrous) hydrofluoric acid, to give monofluoro-, difluoro-, and hexafluoro-phosphoric acid, according to the proportions of the reactants.[24] The reaction is reversible so that, *e.g.*, the monofluorophosphoric acid is completely decomposed on boiling in aqueous solution; but when only a limited amount of water is present, an equilibrium is set up which is very sensitive to the amount of water.[25] With sulphuric acid the situation is very similar, fluorosulphonic acid being formed from hydrogen fluoride and the concentrated acid[26] as noted below (page 124). The dioxides of selenium and tellurium are extremely soluble in LHF[27] and it is suggested that the solid products obtained from these solutions are additive compounds, *e.g.* $SeO_2.5HF$, though in the case of tellurium, oxyfluorides may be formed in the presence of water.[28] Iodine pentoxide shows similar behaviour.[29] The observations of Fredenhagen on the behaviour of chromates and permanganates with hydrofluoric acid have already been noted (see page 124) and in more recent work, chromyl fluoride, CrO_2F_2, and permanganyl fluoride, MnO_3F, have been obtained from potassium dichromate and permanganate.[14] It is suspected that potassium perrhenate gives the corresponding ReO_3F. The action of hydrofluoric acid on metallic chromium and manganese in the presence of potassium nitrate also gave the corresponding oxyfluorides, and with tungsten and molybdenum WOF_4 and $MoOF_4$ were obtained. Chromium trifluoride has been made by dissolving chromium trioxide in aqueous hydrofluoric acid, reducing with sawdust, and evaporating.[30] The formation of uranium tetrafluoride from the dioxide and anhydrous hydrofluoric acid has been considered as a possible manufacturing process.[31]

The behaviour of hydrofluoric acid on electrolysis in aqueous solution has been studied. A dilute solution of the acid, or of various fluorides, was electrolyzed at smooth platinum electrodes, stirred, and the current-voltage curve was plotted.[32] For all the solutions a break occurred at 1·62 V. which was considered to be the decomposition potential of water. A second break occurred, different for different solutions but reproducible for each: for 0·1 N-HF, it was at 1·99 V. at 0°C., for 0·045N-LiF, 2·56 V. at 0°C. Only hydrogen and oxygen were evolved, no fluorine was observed in the anodic products, and the higher break is, presumably, to be attributed to overvoltage effects and resistance in the electrolyte, and not to anything in the nature of a decomposition voltage of the solutes. A later worker[33] made similar determinations with generally similar results, but he concluded that he was observing true decomposition potentials. Later[34] the same author, measuring the overvoltage of hydrogen and oxygen in dilute (0·2N.) hydrofluoric acid, found that for current densities up to 0·005 amp./cm.^{2} Tafel's equation, $V = a + b \log i$, was obeyed while at higher current densities the overvoltages observed were increasingly greater than those given by the equation. The overvoltage phenomena are generally the same as in other common acids, except where the weakness of hydrofluoric acid may exert an influence. Again it is concluded that the second break in the electrolysis curve is to be attributed to some effect other than the decomposition of water.

There has been some discussion as to what happens when aqueous hydrofluoric acid is electrolyzed. Moissan said that ozone is formed by liberation of fluorine and its subsequent reaction with water (see page 55). Briner and Tolun[35] have, however, pointed out that this is a fallacy: strong (40%) acid was electrolyzed at low temperatures, and ozone was produced, though not so much as when sulphuric acid is electrolysed; there was no fluorine or fluorine derivative in the gases evolved at the anode. The formation of ozone is in each case due to free hydroxyl ion discharge, which, even at the very low concentrations occurring in strongly acid solutions, must take place at a potential difference much less than that required for fluoride ion discharge. Thus for values of $[OH^-]$ of 10^{-7} (neutral), 10^{-14} (N-acid) and 10^{-15} (10N-acid) the discharge potentials for hydroxyl ion are 0.81, 1.21 and 1.27 V., whilst the normal discharge potential for fluorine is 2.85 V. Fluoride ion has been shown to have a catalytic effect on certain electrolytic processes. Thus in the electrolytic oxidation of chrome alum to potassium dichromate and in the production of potassium perphosphate the yields are increased by adding potassium fluoride,[36] and in the deposition of metallic chromium from chromic acid solutions additions of hydrofluoric acid increase the current efficiency.[37] The presence of hydrofluoric acid also influences oxidation-reduction potentials, *e.g.* in the case of iron (ferric/ferrous), owing to complex formation.[38]

A curious action of anhydrous hydrofluoric acid has been reported in the formation of graphite bifluoride:[39] when graphite is oxidized in this medium *e.g.* by addition of potassium dichromate, by passing in fluorine gas or by electrolytic action, a blue product is formed, analysis of which indicates a composition represented by $[C_{24}]^+HF_2^-,4HF$. Hydrofluoric acid also exerts a catalytic influence on the formation of carbon monofluoride[40] and is essential in the formation of tetracarbon monofluoride.[41]

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HYDROFLUORIC ACID IN ORGANIC CHEMISTRY

The work of Fredenhagen and Klatt on the solvent properties of hydrofluoric acid for organic compounds has already been mentioned, but this has had, as yet, no further applications. The use of hydrofluoric acid in making organic fluorine compounds by exchange with other halogens has also been referred to. This type of reaction was extensively used in America during the 1939–45 war[1] in attempting to make fully fluorinated compounds. The addition of hydrogen fluoride to olefinic and acetylenic compounds has also been studied; in this way acetylene readily gives vinyl fluoride and ethylidene fluoride, and higher compounds show similar reactions.[2,3,4] Mercury salts are usually used as the catalyst, and on this there are a number of patents,[5] although aluminium fluoride or oxide has also been used[6] and chlorinated olefines have been caused to react with hydrogen fluoride using stannic chloride as catalyst.[7] There have been considerable developments in the use of hydrogen fluoride as a catalyst: it acts generally as does aluminium chloride, sulphuric or phosphoric acid, or boron trifluoride, but has certain advantages in that it can readily be removed from the system by distillation, that tar formation does not occur as with aluminium chloride and that substitution does not occur as with sulphuric acid. The earliest patent in this field was for the use of hydrofluoric acid as a catalyst in cellulose acetylation,[8] but its use has more particularly developed in the petroleum industry, and a good deal of work has been done by J. H. Simons on the catalysis of a great variety of condensation reactions,[9,10,11] though others have also contributed[12] including Russian workers,[13] and there has been great interest in the isomerization of hydrocarbons.[14] The subject has been reviewed by Simons in his book on Fluorine Chemistry.[9] There has been much patent activity in this field relating to hydrocarbon alkylation, isomerization and reforming;[15] and methylation using methyl chloride has been claimed.[16] The catalyst is usually anhydrous hydrofluoric acid and, as has been said (see page 81), much interest has been focussed on the recovery of the catalyst; though admixtures have also been claimed such as aqueous hydrofluoric acid,[17] fluoboric acid[18] and hydrofluorides.[19] The aqueous acid has also been claimed as a catalyst for ring-closure.[20] Hydrofluoric acid has also been used in the treatment of lubricating oils[21] and coal tar distillates,[22] for desulphurizing oils[23] and in cracking.[24] It has been proposed as a catalyst for the addition of hydrogen sulphide to olefines[25] and of organic disulphides to olefines,[26] and other catalytic reactions including olefine hydration,[27] the addition of carbon monoxide ro aromatic hydrocarbons,[28] the oxidation of organic compounds,[29] the mercuration of benzene,[30] the production of lubricants by polymerization reactions[31] and the softening of resins.[32]

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CORROSIVE PROPERTIES AND HANDLING OF HYDROFLUORIC ACID

Consideration of the handling of hydrofluoric acid and the containers in which it is kept and transported follows naturally after a review of the way in which it behaves towards various possible materials, and the available information on corrosive properties must first be examined.

NON-METALLIC MATERIALS

Amongst the non-metallic materials, the first is glass, and the attack of of hydrofluoric acid on this is well known. Mellor states that glass is not affected by the liquid if moisture is absent, but the authority for this is not obvious and it is doubtful whether any acid of low moisture content had been made at that time. Fredenhagen, the first to study critically the moisture content of the pure acid, showed that fused silica ware was resistant to anhydrous hydrofluoric acid and used this fact in his work: it is unlikely that he would have overlooked the fact if indeed glass had been sufficiently resistant. Moissan found that even minute traces of hydrofluoric acid vapour present in fluorine slowly attacked glass. The rate of attack by aqueous hydrofluoric on glass has been studied, and the effect of adding other acids in causing an increased attack is found not to be explicable on the basis of the increase of acidity.[1] The presence of small amounts, possibly unsuspected, of hydrofluoric acid, may, it has been suggested, introduce errors in analytical work by altering the calibration of analytical glassware through corrosion, *e.g.* in the analysis of phosphates containing fluorides.[2] Numerous proposals have been made for protecting glassware from attack; a Russian patent claims a mixture of ceresine, resin and tar[3] and special procedures in waxing glass bottles have been protected,[4] including the application of special waxes in an organic solvent.[5] We may note here that Roth attempted to use waxed glass containers for thermochemical work on aqueous hydrofluoric acid, but found that slight penetration of the wax lining permitted some attack on the glass. Thorvaldson and Bailey, in their work on the specific heat of aqueous hydrofluoric acid, used waxed glass vessels for titrations, but their calorimeter was made of gold. As an alternative to glass, a porous ceramic container impregnated with wax has been proposed.[6] In recent years special glasses with pronounced resistance to aqueous hydrofluoric acid have been made. An early patent claims a glass composed of oxides of aluminium, phosphorus and alkali metals, but free from silica[7] and a later patent claims an aluminium phosphate base (P_2O_5 60 – 85%, Al_2O_3 10 – 20%) with additions of oxides of zinc, beryllium or lead up to 30%, and a fraction of one per cent of lithia.[8] The behaviour of laboratory glassware made of these materials has been described.[9] The glassware has been marketed under the trade name 'Fluorex' and tests indicate that when it was exposed to 48% acid for 24 hours the rate of loss in successive tests was 0·389, 0·241, and 0·212 mg./cm^2/hr., and the glass remained unfrosted and clear.[10]

The use of silica glass by Fredenhagen[11] has been mentioned; in studying the rate of attack of aqueous acid on silica[12] it was found that this is determined not by the free acid molecules present, but by the fluorine-containing ions. In the corrosion of quartz crystals, the rate of attack varies with the crystal face exposed and is increased by *X*-ray irradiation.[13] Studies have been made of the attack of aqueous hydrofluoric acid on various micas, where etching can produce either regular patterns or general disintegration and the rate varies widely with materials from different sources.[14]

Though there have been considerable developments in organic materials, gutta percha still serves as a material for bottles for strong aqueous hydrofluoric acid.[15] Rubber lining is resistant to the aqueous acid, and various types are now used.[16] In a quantitative study, ebonite after eight weeks

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exposure at 20°C. gained 1·62% in weight in 6% hydrofluoric acid, compared with losses of 0·03% in 25% sulphuric and 0·014% in strong hydrochloric acid.[17] As regards wax, whilst there are no specific investigations of the resistance this seems to be good, and wax is much used in making bottles for hydrofluoric acid.[18] Considering the newer polymeric materials, it has already been seen, in Fredenhagen's work on the solvent properties of LHF, that when organic compounds polymerized the polymer was precipitated from solution; many available polymers are not attacked either by aqueous or anhydrous acid and several examples of their use have been given. In a careful quantitative study of the action of 48% acid it has been shown that urea-formaldehyde resins and cellulose acetate are soluble, that phenol-formaldehyde and melamine-formaldehyde resins are attacked and that polymethyl methacrylate swells. On the other hand polyethylene, and a copolymer of vinyl chloride and vinyl acetate, are hardly affected, and polystyrene shows outstanding resistance.[19] It has been noted above that a Bakelite vessel was used in determining the densities of aqueous acids; and the use of phenol-formaldehyde, or other suitable resin, with a graphite filler for making containers for hydrofluoric acid, has been patented.[20] Graphite impregnated with a thermosetting resin is sold as 'Karbate' and it is said[16] that this material is resistant to 48% acid up to the boiling point, and to 60% acid up to 85°C., though it is not recommended for acids stronger than 65%. Polymethyl methacrylate was used by Roth for his work on indicators in dilute hydrofluoric acid, and an announcement of the value of a German product of this type, 'Plexiglas', was made at the time.[21] Later a polystyrene product, 'Trolitul', available in plates, rods, and tubes, glass clear, was recommended for use with the anhydrous acid.[22] Reference has also been made to a French material 'Duroid', resistant to 40% acid, as well as to alumina, for use in optical work.[23] Attention has been drawn also to the value of amber, which can be hot-pressed into test tubes and other forms, for its resistance to 50% hydrofluoric acid.[24] The silicone polymers are of no use in hydrofluoric acid as they are attacked and give rise to volatile products, the attack being greater with the anhydrous acid.[16]

METALLIC MATERIALS

A number of reviews deal with the general behaviour of metallic materials towards hydrofluoric acid.[16, 25-29] Considering firstly ferrous materials, iron and steel, whilst not resistant to aqueous acid, are satisfactory for acids stronger than 80% and, as has been seen on pages 29,32, mild steel shows very satisfactory resistance even at higher temperatures,[29] and is generally used in large scale equipment for the handling and production of anhydrous acid. The rate of corrosion of a low carbon steel at elevated temperatures by anhydrous acid, penetration in inches per month, is 0·051, 0·048, 0·025 at 500, 550, and 600°C. respectively:[28] no explanation is given of the apparent fall of the corrosion rate with rising temperature. Some comparative observations on the corrosive attack on steel by hydrofluoric acid and other chemicals have been reported.[30] When hydrofluoric acid is used in etching ferrous materials, characteristic 'barley shell' markings are produced which are attributed to the influence of ferrous fluoride crystallizing out and not to the structure of the alloy.[31] When iron is exposed to aqueous fluoride solutions, protective films reduce the rate of attack.[32] Among the ferrous alloys high-silicon irons, normally highly resistant to acid attack, do not resist aqueous hydrofluoric acid.[16] The stainless steels are said to be subject to the pitting type of corrosion, and are to be avoided[29] except possibly for anhydrous acid,[16] in which, it is said, the addition of nitric acid completely inhibits attack. Some results of high temperature tests have been given (in Table XXXIV), but are not very concordant:

TABLE XXXIV.- CORROSION OF STAINLESS STEELS[28]

Alloy No.	Nominal composition			Penetration, in./month at		
				500°	550°	600°
430	14 – 18%Cr.		remainder Fe	0·005	0·030	0·038
304	18/8	Cr/Ni.	remainder Fe	–	–	0·044
347	18/10	Cr/Ni +Cb.	remainder Fe	0·6	1·5	0·58
309Cb	25/12	Cr/Ni +Cb.	remainder Fe	0·019	0·14	0·55
310	25/20	Cr/Ni.	remainder Fe	0·04	0·33	1·0

Some figures obtained for other metals in the same high temperature corrosion test are given in Table XXXV.

TABLE XXXV.- HIGH TEMPERATURE CORROSION TESTS[28]

Metal	Nominal Composition	Penetration, in./month at	
		500°	600°
Nickel		0·003	0·003
Monel	70/30 Ni/Cu	0·004	0·006
Copper		0·005	0·004
Inconel	80/14/6 Ni/Cu/Fe	0·005	
Aluminium 2S	2% Mn	0·016	0·005
Magnesium	Dowmetal G	0·042	0·048

There can be no doubt about the good performance of the nickel alloy, and generally nickel and monel are said to be the best metals for resistance to hydrofluoric acid[16, 25, 27, 28] although copper also shows very high resistance.

The rate of corrosion in mixtures of water vapour and hydrofluoric acid is given below,[28] and is of the same order as in pure hydrofluoric acid:-

	Rate of penetration, in./month at				
	550°	600°	650°	700°	750°
Monel	–	0·002	0·005	0·013	0·017
Nickel	0·0026	0·006	0·009	0·012	0·010

Other complex alloys containing nickel and various other alloying metals, 'Hastelloys', 'Chlorimets', 'Durimets', show good resistance even to aqueous acid, although in some cases the Hastelloys may corrode badly.[16]

Aluminium is corroded by aqueous hydrofluoric acid[16] but an alloy with 2% of manganese is reasonably resistant to the vapour of the anhydrous acid at 500 and 600°C. as shown in Table XXXV above. The acid has been used in etching pure aluminium.[33] Magnesium and its alloys are generally said to be very resistant to all strengths of hydrofluoric acid[34] but attack may occur when sulphuric acid and hydrofluosilicic acid are present.[35] The influence of fluorides on the corrosion of magnesium in chloride solutions has been studied.[36] Tantalum is rapidly attacked[16] and hydrofluoric acid has been proposed for use in its electrolytic polishing;[37] titanium suffers some attack by aqueous acids;[38] silver is unattacked by cold 46% acid[39] and ranks in resistance with platinum and monel.[27] Lead is resistant up to the boiling point at strengths of acid not exceeding 60%, but above this shows some attack.[28]

From this review of the handling of aqueous or anhydrous acid it is obvious that a variety of materials is available and that in laboratory work, in spite of the attack on glass and notwithstanding a contrary opinion relating to work with the anhydrous acid,[40] there are various solutions to the problem of 'seeing what happens.'

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HANDLING OF HYDROFLUORIC ACID

The handling and transport of hydrofluoric acid were discussed quite briefly by Mellor (II, 128): it had been recommended that the anhydrous acid be kept in platinum bottles, but this was too expensive and ceresine wax bottles were generally used. The commercial (aqueous) acid was bottled and sealed in lead, gutta percha, paraffin or ceresine wax bottles.

A clear distinction must still be drawn between the anhydrous acid and aqueous solutions, for two reasons: the difference in boiling point and the very different corrosive properties. Because of its low boiling point, the anhydrous acid must be treated, according to British regulations, as a liquefied gas for transport purposes and so must be kept in containers which can withstand an appreciable pressure. The aqueous acid, on the other hand, has no very great vapour pressure at any temperatures likely to be met with in ordinary circumstances, and its containers are subject to no such requirement. As regards corrosion in relation to handling, it has been pointed out that the anhydrous acid is an entirely different material from the aqueous acid,[41] and that between 60% and 80% strength the corrosive effects change very greatly. Below 65% the corrosion of lead is low, but the rate of corrosion increases rapidly above this strength. Below 60% the attack on steel is very considerable whilst above 80% there is no appreciable attack. Rubber, neoprene and many plastics are excellent in weak acid, but are increasingly attacked above 60% strength.

The anhydrous acid, normally material of 98% strength or greater although it can include material with 80% only of hydrogen fluoride (which is a strength made in one works in the U.S.A. and shipped to another works for rectification), is shipped in steel cylinders and tank wagons which in Great Britain come under the Regulations for liquefied gases.[42] These vessels may be designed for taking off the vapour, or with a dip-pipe so that liquid can be withdrawn through the valve.

For the aqueous acid, which is shipped in various strengths up to 65%, a variety of containers may be employed, and these have been described for American practice.[43] The weaker acids, up to 30%, may be shipped in wooden barrels, which must be asphalt lined and tested before use to withstand a pressure of 5 lb./sq.in., or in tank cars, similarly lined. Rubber lined vessels may be used for strengths up to 40%, and lead carboys or rubber lined drums up to 65%. For small quantities, containers of rubber, ceresine, lead 'or other material resistant to hydrofluoric acid' (such as polyethylene) are permitted but must be packed in a wooden box. Between 60% and 80%, drums and tank wagons of plain steel may be used, but they must be 'passivated' (rendered passive) by previous exposure to acid. This treatment has been patented[44] and consists in filling the iron vessels to 90% capacity with 58% acid and allowing them to stand for 48 hours at 27°C. and then for 7 hours at 60°C.

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THE USES OF HYDROFLUORIC ACID, FLUORIDES, AND OTHER FLUORINE COMPOUNDS

Only a brief condensed survey of this field can be given; further information may be found in technological encyclopaedias *e.g.* 'Kirk-Othmer'.[1] Calcium fluoride, as already seen, is the main source of fluorine compounds in industry, although natural cryolite is extensively used, and the recovery of fluorine, usually as fluosilicate, from phosphate rock processing is yet another source of fluorine. Calcium fluoride is either converted to hydrofluoric acid or used directly, in the iron and steel industry and in other metallurgical processes, welding, etc. as a fluxing agent. Another considerable use is in glass and vitreous enamels; the clear variety is used for ornamental purposes, and synthetic crystals clear enough for optical purposes are now made. Hydrofluoric acid is used for making most of the other fluorides needed in trade and in industry, and for making organic fluoro-derivatives: and much is needed for the Atomic Energy industry, where the use of uranium hexafluoride calls for fluorine and fluorine-resistant materials. It is used also as a catalyst in the petroleum industry, mainly for the production of 'alkylate', a mixture of heptanes and octanes of high 'octane number', from olefines and butanes. It is used for making aluminium fluoride and synthetic cryolite for the aluminium industry. Hydrofluoric acids of various strengths are of course used for etching and frosting glass and the concentrated aqueous acid is used for 'polishing' cut glassware. Boron trifluoride has become available commercially, as a compressed gas in cylinders or as an additive compound, *e.g.* with ether, water (fluoboric acid) etc.; it has aroused much interest as an organic catalyst and for the preparation of organic compounds, and the fluoborates have found special uses in the metal industry and, for example, in electrodeposition baths, for nickel and other metals. Hydrofluosilicic acid and its salts have found applications as disinfectants, as insecticides and fungicides, in tanning, and in electroplating and refining. Fluorosulphonic acid has proved of interest as an organic catalyst, for use in organic preparations, and in electrochemistry. A number of inorganic fluorides, including those of sodium, potassium, barium, magnesium, and lithium, are useful as fluxes, as heat treatment salts and for other similar purposes in metallurgical industry and in the glass and enamel industries. Beryllium fluoride is used as a molten bath in the production of beryllium, chromium trifluoride is used as a mordant in dyeing, and rare earth fluorides are used in arc lamp carbon cores. Sulphur hexafluoride has been proposed as a valuable gaseous dielectric because of its high breakdown voltage.

Among organic compounds, there has been extensive development of the simpler fluorochlorocarbon compounds, marketed as 'Freons' and 'Arctons'. The stability, inertness and volatility of such compounds as difluorodichloromethane, CF_2Cl_2, has led to their use as propellants for aerosol insecticides, and, developing from this, for many like purposes such as spraying paints, floor waxes, cosmetics and perfumes. The first development of these compounds was of course as refrigerants, and this application has expanded very considerably. Through such derivatives as benzotrifluoride, fluorine has found some applications in dyestuffs, and the polymers of tetrafluoroethylene ('Teflon', 'Fluon') and of trifluorochloroethylene ('Kel-F',[2] 'Fluorothene')[3] have been found of great value for certain uses. Fluorocarbon lubricants and fluorochlorocarbon lubricants have been developed, especially for the Atomic Energy industry.

Fluorides are used, or proposed for use, for a variety of reasons in vitreous enamels and in the glass industry.[4] In vitreous enamels[5] the principal compounds used are cryolite, fluosilicates, and calcium and sodium fluorides, mainly for their opacifying effect[6] though they are beneficial also for their assistance in fluxing the frit.[7] The opacifying action is said to be due to crystallization rather than to the formation of gas bubbles[8] though volatilization, giving rise to losses, does occur.[9] The colour imparted to enamels by iron oxide depends on the proportion of fluoride present.[10] A ceramic lining made from fluorspar[11] and capable of withstanding a temperature higher than 1200°C. is rather outside the class of enamels. The production of refractory ware from calcium fluoride, which has been mentioned as of use in the preparation of fluorine, has been the subject of a recent Russian patent.[12] In the glass industry, fluoride additions act as accelerators of the melting process,[13] reduce the viscosity of the melt[14] and may also provide an opacifying action as in enamels.[15] A decolorizing action of sodium fluoride additions has also been suggested.[16] The use of fluorides in this field has been generally reviewed.[17] The addition of fluorides and other elements to give special optical glasses has been proposed,[18] including an all-fluoride glass.[19] The uses of fluorides and particularly hydrofluoric acid for engraving[20] and frosting[21] glassware, and in graduating scientific glassware[22] are well known. More recent developments of the superficial use of fluorides on glass have been in the direction of reducing the reflection and glare from glass surfaces in optical systems[23] and an unusual one is the strengthening of glass bottles by hydrofluoric acid treatment.[24]

In the cement industry, fluoride additions have a mineralizing action[25] and a series of studies has been reported of this effect on individual mineral formation:[26] it may be related to the mineralizing action in geochemistry.[27]

The closely adherent oxide coat formed on aluminium and its alloys in appropriate circumstances is of great value in imparting corrosion resistance. The development of magnesium alloys for constructional purposes, which began in the 1920's, opened up the question of preventing corrosion with this metal also. Unfortunately the oxide film does not protect magnesium, and in the 1930's there was marked activity, mainly in the patent field, relating to the production of fluoride films on magnesium. Dipping processes were inadequate[28] and recourse was had to anodic treatment in a variety of baths. Molten baths of low melting salts such as potassium bifluoride were proposed[29] to which various additions such as boric oxide[30] or urea[31] were made; or the bath might contain more hydrofluoric acid, up to $KF,4HF$, or might consist of ammonium acid fluoride up to $NH_4F,5HF$[32] or of the acid hydrofluorides of organic bases;[33] or aqueous,[34] alcoholic or polyhydric alcohol[35] solutions of neutral highly soluble fluorides might be used. The coatings so obtained may require subsequent treatment with wax, lacquer etc. to seal the pores.[36] Fluorides have also been proposed for the protection of magnesium against corrosion in a special case.[37]

It has already been seen, under the occurrence of fluorine, how attempts have been made to rectify the errors of Nature so far as the fluorine content of drinking water is concerned. This has led to another use for sodium fluoride or fluosilicate[38, 39] and to trouble in making ice from treated water.[40] For insecticidal uses the water-insoluble double fluorides of aluminium and the alkali metals[41] have been suggested. For wood preservation, sodium fluoride and sodium fluosilicate are used, though other salts have been proposed.[42-44] Hydrofluoric acid has been used as a preservative for fruit juices, and this practice has been attacked and defended.[45, 46] The use of fluorides and fluosilicates to protect wool against clothes moths has also been considered[47] In the processing of wool, treatment with elementary fluorine has been claimed to have a beneficial non-felting effect.[48-50] Hydrogen fluoride[51-53] and fluorides[54] have been found useful for activating catalysts, in photographic print material,[55, 56] in phosphors;[57, 58] to improve the strength of asbestos paper,[59] to give silica-free powdered iron,[60] to increase the flow of oil wells,[61] in making a micaceous insulator,[62] as a defoliant[63] and in the production of fresh water

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from sea-water.[64] Fluorides have assisted in cleaning evaporator tubes,[65] in the coagulation of rubber[66] and in the production of persulphates.[67] The use of fluorides in metallurgical industry has been described,[68] and in the steel industry it has been suggested that they lead to removal of sulphur.[69] The use of hydrofluoric acid for liberating other acids has been proposed[70] and possible new uses of fluorides in industry have been discussed.[71] In organic chemistry, fluorides have been proposed to assist recovery in a nitration process[72] and certain uses for fluorinated hydrocarbons have been claimed.[73] The properties of the plastic Kel-F, polytrifluorochloroethylene, have been described.[2,3] Recently it has been stated that the output of hydrofluoric acid in the U.S.A. is expected to rise to 60,000 tons per annum by 1955, and that the large uses will include production of high octane fuel; pickling stainless steel; refining rare metals; making 'Freons' for refrigeration; air conditioning; plastics; aerosol propellants; and atomic energy requirements.[74]

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SECTION V.

COMPOUNDS OF FLUORINE WITH CHLORINE, BROMINE AND IODINE.

By H. R. LEECH

THE HALOGEN FLUORIDES

In the original Treatise, Mellor said that fluorine and chlorine form neither compounds nor mixed crystals, and it was indeed true that no compound of fluorine with chlorine had then been reported. The only halogen fluorides described at that time were the trifluoride of bromine and the pentafluoride of iodine. Since then two chlorine fluorides, two more bromine fluorides and another iodine fluoride have been prepared (Table I), all being first reported by Ruff and his colleagues between 1928 and 1934.

TABLE I.- THE HALOGEN FLUORIDES

Compound		Date	m.p. °C.	b.p. °C.
Chlorine monofluoride	ClF	1928	–155·6	–100·1
Chlorine trifluoride	ClF_3	1930	–76·3	+11·75
Bromine monofluoride	BrF	1934	–33	+23
Bromine trifluoride	BrF_3	1891	+8·77	125·76
Bromine pentafluoride	BrF_5	1931	–61·3	.40·5
Iodine pentafluoride	IF_5	1871	+9·6	98
Iodine heptafluoride	IF_7	1930*	+5–6	4·5

* but see below

As will be seen below, Ruff had gone to a great deal of trouble to try to combine fluorine and chlorine. The simplest and easiest way to cause chemical reaction is to heat the reactants, and in fact fluorine and chlorine combine explosively when so treated: fluorine reacts immediately with bromine and iodine at ordinary temperatures, and the higher fluorides are readily made by further action of fluorine at about 250°C. on the lower fluorides first formed. It is essential to use dry materials and apparatus, and the fluorine must be freed from hydrogen fluoride by methods which have already been described. These halogen fluorides are now all well characterized with the exception of bromine monofluoride, which is unstable and on the existence of which some doubt has been cast.[1] They are all very reactive compounds, with properties in many respects very similar to those of fluorine. They react violently with water and with organic compounds containing much hydrogen; they will react with most oxidizable materials in appropriate circumstances, but they can quite readily be handled in steel equipment at ordinary temperatures. The materials that may be used in handling the halogen fluorides are in general the same as for fluorine (q.v.) although in certain cases these compounds may be more corrosive than fluorine itself.

In recent years chlorine trifluoride and bromine tri- and pentafluoride have become commercially available,[2] and several workers have referred to the use of these commercial supplies; iodine pentafluoride has also been obtained commercially.[3] These compounds may be expected to become valuable reagents as their properties become more widely known. Some of them have already become of special interest, as will be seen below: chlorine trifluoride was to be made on a scale of 1000 tons annually in Germany during World War II; bromine trifluoride has been found to show particularly interesting solvent properties, iodine pentafluoride has been of value in the preparation of perfluoroalkyl halides, which are useful in synthetic fluorocarbon chemistry. A number of reviews of the halogen fluorides have been published in recent years[1,2,4] as well as lectures and discussions.[5,6] Sidgwick has discussed steric factors arising in the formation of the compounds,[7] this subject having also been considered earlier by Ruff.[8]

CHLORINE MONOFLUORIDE

In his book 'Die Chemie des Fluors', published in 1920, Ruff tried to estimate the probable heat of formation and volatility of chlorine fluoride, which he said could be expected to be ClF.[9] He concluded that the heat of formation was likely to be greater than -8 kg.-cal., so that the stability of the compound would be about the same as that of hydrogen iodide or possibly greater. It was estimated that the boiling point of such a compound would be about -100°C., and unsuccessful attempts to prepare it were described. Chlorine in a nascent state, produced in as many different ways as possible, was caused to react with fluorine.[10] In this way it was found that there was an extraordinarily violent reaction between dry hydrogen chloride and fluorine, and in making rhodium fluoride from the chloride and fluorine, some explosions occurred. When chlorine was introduced into fluorine, and heat was applied at the point of introduction, a pale flame was observed and much heat was evolved, but the compound so formed evaded isolation. When, however, hydrogen chloride gas was passed into liquid fluorine, there was a green flame, a mist was formed, and white flakes sank to the bottom of the vessel. From this mixture it was possible to isolate a compound boiling between -80° and -110°, and it was then found that the compound could more readily be made by mixing chlorine with fluorine in a copper vessel heated to 250° and carrying out a fractional distillation on the product condensed in liquid air.[11] A colourless gas with a strong odour was obtained which condensed in liquid air to a white solid, m.p. -161°, b.p. -103° C.; the reactions of this compound were similar to those of fluorine, but in some cases, especially with arsenic and antimony, more vigorous. Shortly after this discovery Fredenhagen and Krefft described experiments on the sparking of fluorine-chlorine mixtures in a gas bulb.[12] A yellowish-red flame spread through the vessel on sparking, and when the gases were present in suitable proportions there was a violent explosion. If, on the other hand, the vessel was thoroughly dried by strongly heating in a stream of dry air, a flame could be produced on sparking fluorine-chlorine mixtures in it but there was no explosion; admission of a trace of moisture, however, again gave rise to explosive reactions. These authors thought that Ruff was wrong in suggesting that an equilibrium,

$$Cl_2 + F_2 \rightleftharpoons 2ClF$$

was established; they held that the explosions indicated that the two reactants must have a strong affinity and that combination must be essentially complete. About this time Ruff was able to demonstrate the combustion of fluorine in chlorine as a lecture experiment; a vessel of lead glass filled with chlorine had an internal jet delivering fluorine, the jet being wound with a platinum wire electrically heated to ensure the initiation and continuance of combustion.[13]

CHLORINE MONOFLUORIDE: PREPARATION

Ruff's method of passing the mixed gases in the correct proportions through a copper tube at 250°C. is eminently simple; it has been used more recently and a temperature of 220–230°C. has been recommended.[14] The reaction of chlorine trifluoride with an equal volume of chlorine under similar conditions has been used,[15] and now that chlorine trifluoride can be purchased, this offers a ready means of making the gas. A third method used by the same authors, of fractionally distilling the monofluoride from a cylinder of commercial chlorine trifluoride, in which they find appreciable quantities of the monofluoride occur as impurity, seems to reflect adversely on the quality of the supply. Other workers have acknowledged the gift of supplies of the gas from chemical manufacturers.[16] The interaction of chlorine monofluoride and fluorine in equilibrium with the trifluoride will be discussed under that compound, but it may be noted here that the thermal dissociation of the trifluoride, which has been used as a source of fluorine, may equally be regarded as a source of chlorine monofluoride, although the reaction of the trifluoride with chlorine discussed above is perhaps more economical.

CHLORINE MONOFLUORIDE: PHYSICAL PROPERTIES

The m.p. of chlorine monofluoride is −154° ± 0·5,[17] −155·6°;[18] the b.p., −100·8°,[17] −100·1°;[18] the vapour pressure, determined between −150° and −105°, is given by $\log p_{\text{mm.}} = 15{\cdot}738 - \frac{3109}{T} + \frac{1{\cdot}538\times10^5}{T^2}$.[17] The density at the boiling point is 1·62.[18] Ruff and Laass gave 2·27 kg.-cal. for the molar latent heat[17] but in a later paper stated that this was in error.[19] The recalculated value was 4·8 kg.-cal., from which the value of Trouton's constant was 28·0. This figure is abnormally high and, together with evidence that their chlorine monofluoride was contaminated with trifluoride, convinced Ruff that the vapour pressure needed to be redetermined. There is no record of this having been done, but in a more recent critical compilation the latent heat is given as 5·34.[20] The thermodynamic properties have been calculated from the spectrum of the compound[21] and are given in Table II.

Some comparable data, differing very slightly from those in Table II, have been calculated from the Raman spectrum.[22] The thermochemistry has, not unnaturally, been given some attention. As has already been seen, Ruff thought that in heat of formation and stability the compound might be like hydrogen iodide, and it was thus, perhaps, that he was led to look for an equilibrium reaction in its formation, which Fredenhagen pointed out was wrong. The first experimental determination of the heat of formation of chlorine monofluoride by Ruff and Laass gave 24·7 kg.-cal.[17] later corrected to 25·7 kg.-cal.[23] A calculation of the dissociation energy to the ground state, from spectral data, led to a value of −60·31 kg.-cal., which could not be reconciled with the heat of dissociation of chlorine, the above heat of formation, and the then accepted figure for the dissociation energy of fluorine.[24] It was concluded that the dissociation energy of fluorine must be lower than was believed, and the heat of formation of chlorine monofluoride less than the values so far determined. The spectral value given above for the dissociation energy has been confirmed,[25] and the thermochemistry of the reaction between chlorine monofluoride and sodium chloride further studied.[26] The reaction proceeds smoothly in silica, there is no trace of fluorine in the exit gas, and the mean of ten determinations gave $NaCl + ClF \rightarrow NaF + Cl_2 + 24{\cdot}5$ kg.-cal. ± 0·1 at 18°C. (In the same paper, for the corresponding reaction with fluorine a value of 39·5 ± 0·5 kg.-cal. was obtained, where von Wartenberg had obtained 39·3 kg.-cal. (see page 62)). This gave for the heat of formation of chlorine monofluoride at 18°C., 15 ± 0·5 kg.-cal., which is very different from the value

TABLE II. - THERMODYNAMIC FUNCTIONS[21] OF ISOTOPIC ClF

T°K	$-(F^\circ-H_0^\circ)/T$ g.-cal./deg.mole	S° g.-cal./deg.mole	C_p° g.-cal./deg.mole
298·16	44·904	52·045	7·672
300	44·948	52·092	7·680
350	46·056	53·292	7·895
400	47·029	54·358	8·072
500	48·684	56·189	8·348
600	50·067	57·731	8·534
700	51·259	59·057	8·666
800	52·308	60·221	8·762
900	53·246	61·257	8·836
1000	54·094	62·191	8·894
1100	54·870	63·041	8·942
1200	55·584	63·821	8·983
1300	56·245	64·542	9·019
1400	56·862	65·212	9·050
1500	57·440	65·837	9·079
1600	57·983	66·424	9·106
1700	58·496	66·977	9·130
1800	58·982	67·500	9·153
1900	59·444	67·995	9·175
2000	59·883	68·466	9·196

determined by Ruff and Laass. Combining this with the dissociation energy, the heat of dissociation of fluorine is either -30·6 or -33·4 kg.-cal. A value of 11·6 kg.-cal. ± 0·4 has been obtained by measurement for the heat evolved in the reaction of fluorine and chlorine.[27] The question is further discussed under chlorine trifluoride where it is shown that 11·6 kg.-cal. is the most likely value. It has also been concluded that the bond in this compound is 20% ionic, 80% covalent.[16]

CHLORINE MONOFLUORIDE: CHEMICAL PROPERTIES

As regards the chemical properties of chlorine monofluoride, there has been little study, and what is known suggests that much awaits discovery. Ruff gave some general properties,[10] but these data are not too reliable in the absence of precise information on the state and purity of the reactants and the conditions of the reactions; this is, for example, clearly shown in the influence of traces of moisture on the formation of chlorine monofluoride. Ruff stated that the gas attacks glass, leading to the formation of chlorine monoxide from the silica, $4ClF + SiO_2 \rightarrow 2Cl_2O + SiF_4$, but more information on the dryness of his apparatus is desirable. He stressed the general similarity of the reactions of chlorine monofluoride and fluorine, both being outstanding in their attack on moist materials and on most common organic compounds. He stated that the compound was less reactive towards sulphur than was fluorine, but it was more reactive to cotton wool and to metals.[13] The general handling and manipulation of chlorine monofluoride is similar to that of fluorine (q.v.). In work on the spectrum, fused silica has generally been used, but the use of cells machined from 'Fluorothene' (polytrifluorochloroethylene) and provided with rock salt windows has been described.[15] The rock salt windows were attacked, slowly at low pressures, more rapidly at higher pressures, and the infra-red transmission of the windows was affected.

The reaction of chlorine monofluoride with carbon monoxide has been described;[28] when the gases are mixed, using excess of the latter, at -18° in an iron vessel carbonyl chlorofluoride, COClF, is obtained in 85 - 90% yield. In the same circumstances chlorine trifluoride gives a yield of only 10%. Carbon monoxide also reacts with bromine trifluoride and iodine pentafluoride to give the carbonyl bromo- and iodo- fluorides.

CHLORINE TRIFLUORIDE

When Ruff was determining the heat of formation of chlorine monofluoride, he took successive portions of the compound from a bulk sample condensed in liquid air, and found a systematic increase in the values obtained for the heat of reaction. He was led to suspect the presence of a less volatile compound and by fractional condensation of the product from the reaction of fluorine and chlorine, supplied at the rate of 1200 cc. and 800 cc. per hour respectively in the chlorine monofluoride reactor, Ruff and Krug were able to separate this compound and characterize it as chlorine trifluoride.[19] The composition and many physical and chemical properties were given at the same time.

CHLORINE TRIFLUORIDE: PREPARATION

The reactor used for this work was of copper, which has also been used in later reactors.[2,14] The outstanding resistance of copper to fluorine, at 350°C. and even higher, has already been noted. But Ruff and Giese, in pointing this out, said that the addition of chlorine to the fluorine accelerates the reaction between metal and fluorine considerably.[29] It may therefore be inadvisable to use copper, and nickel has been used.[6] This metal was used for a large industrial unit erected in Germany during the war, 1939–45, to make something over 1000 tons per year of chlorine trifluoride, to be used by the German Army, it is stated, in flame throwers and as a general incendiary agent.[30] The fluorine cells and the hydrofluoric acid plant for this project have already been described. The fluorine was compressed to 2 atm., cooled to −60° to remove hydrofluoric acid, and then passed through an orifice flowmeter to give the flow rate to which the flow of chlorine could be adjusted. The fluorine was divided in 1:2 proportion, and the smaller portion was first converted into the monofluoride, to which the remaining fluorine was then added for conversion into trifluoride. The reaction was carried out in three reactors in series, of shell and tube type, made completely of nickel: the chlorine and fluorine were preheated to 200° in nickel heaters and then, once the reaction had started, the reactors were cooled by air blowing. The arrangement of the reactors was such that gradual mixing of the reactants occurred, and one reactor was 10 ft. between tube plates, 28 in. diameter, and provided with ¾ in. tubes at 1⅛" triangular spacing. The overall efficiency of the reaction was 95%. The gases from the reactors were cooled, and the condensed chlorine trifluoride was stored in steel vessels of 5 cu.m. capacity. In connection with their 2000 amp. fluorine cell at Leverkusen, I. G. Farbenindustrie had a small chlorine trifluoride reactor[30,31] which was a Monel metal tube of 1 in. bore, 4½ ft. long, maintained at 250°C. The product was filled into steel cylinders.

Since the publication of the above work on preparation methods, it has been shown that chlorine trifluoride dissociates into the monofluoride and fluorine, to the extent of 4·9% at 300° and increasingly at higher temperatures (see page 154). Thus in any preparation, as some heating is necessary to secure a reasonable rate of reaction, the yield on fluorine must be less than 100%. The yield cannot be increased by increasing the proportion of chlorine; this would only lead to greater production of the monofluoride (which may well explain the reported presence of this compound in some commercial materials). The yield could however be increased by bringing to equilibrium, condensing out the bulk of the trifluoride, and then re-equilibrating.

It has already been pointed out that chlorine trifluoride is available commercially both in U.S.A. and in Great Britain.

CHLORINE TRIFLUORIDE: PHYSICAL PROPERTIES

The properties of chlorine trifluoride were fully described by Ruff and Krug in their first paper on the subject, and the properties have also been given in the reviews referred to above, and in a special compilation.[32] The compound gives dense white fumes in air, and when pure the liquid is almost colourless, although decomposition products – especially from traces of moisture – may lead to development of colour, very pale at first but deepening to dark green and brown.[19] It freezes to a white solid, of which the m.p., first given as -83°C., was later corrected to -82·6°,[18] though a more recent determination of high accuracy gives -76·3°C. (196·84°K).[33] Ruff[19] gave a vapour pressure equation, $\log p_{\text{mm.}} = 7{\cdot}42 - \frac{1292}{T}$, giving a normal boiling point of 11·3°, latent heat of evaporation 5·9 kg.-cal./mole, and critical temperature 153·5°C. The more recent work gives $\log p_{\text{mm.}} = 7{\cdot}36711 - \frac{1096{\cdot}917}{t + 232{\cdot}75}$ [33] and a normal boiling point of 11·75°, which is almost the mean of Ruff's value and another determination of 12·0°.[34] The latent heat of fusion is 1·8193 kg.-cal./mole, while that of evaporation is 6·580 kg.-cal./mole, and data on heat capacity and entropy have also been given.[33] The values here reported for heat capacity of the liquid and for entropy are given in Tables III and IIIa. For the solid at 14°, 62°, 97° and 175°K. the molal specific heat was 1·03, 9·07, 12·10, 17·63; for further data, from 14°K., the original paper should be consulted. There was a transition in the solid at 190·5°K.

TABLE III. - MOLAL HEAT CAPACITY OF CHLORINE TRIFLUORIDE, g.-cal./deg.

T °K.	$C_{\text{Sat'd.}}$	T °K.	$C_{\text{Sat'd.}}$	T °K.	$C_{\text{Sat'd.}}$
196·84	26·68	216·53	26·94	248·61	27·38
202·76	26·76	219·84	26·96	259·30	27·61
204·83	26·78	226·95	27·05	269·86	27·84
207·69	26·81	237·83	27·22	278·25	28·02

TABLE IIIa. - ENTROPY OF CHLORINE TRIFLUORIDE, g.-cal./deg. mole.

$S_{14°}$(3° freedom, $\theta = 102{\cdot}65$)	0·373
$S_{14\text{-}190{\cdot}50°}$ solid,	21·436
$S_{190{\cdot}50°}$ transition,	1·892
$S_{190{\cdot}5\text{-}196{\cdot}84°}$ solid,	0·621
$S_{196{\cdot}84°}$ fusion,	9·243
$S_{196{\cdot}84\text{-}284{\cdot}91°}$ liquid,	10·090
Entropy of liquid at b.p., 284·91°K.	43·66 ± 0·10
$S_{284{\cdot}91°}$ vaporization,	23·10
Correction for gas imperfection	0·11
Entropy of the ideal gas at the b.p.	66·87

Thermodynamic properties of the unassociated vapour at 760 mm. pressure, calculated from the Raman spectrum, are given in Table IV.[22]

The density of the liquid between -5° and +46° is given by $d = 1{\cdot}8853 - 2{\cdot}942 \times 10^{-3}t - 3{\cdot}79 \times 10^{-6}t^2$ g./cc.[34] The specific electrical conductivity is less than 10^{-6} ohm.$^{-1}$ cm.$^{-1}$ at 0°C.[35] Ruff[19] always obtained low values for the vapour density owing to a small amount of reaction with the glass container; three values (H = 2) gave 86·71, 87·49, 87·93 (ClF_3 = 92·46). Subsequent workers, however, from measurements in quartz between 300 and 800 mm. and

TABLE IV. - THERMODYNAMIC PROPERTIES OF CHLORINE TRIFLUORIDE VAPOUR, g.-cal./mole.

T, °K.	$-(F^\circ - H_0^\circ)/T$	S°	C_p°
298	55·52	66·61	15·33
400	58·97	71·35	16·91
500	61·85	75·24	17·81
600	64·35	78·52	18·37
700	66·59	81·38	18·73
800	68·60	83·90	18·98
1000	72·11	88·18	19·29
1250	75·76	92·50	19·49
1500	78·85	96·07	19·60

between 9° and 24°C., have concluded that there is some association, and give values of the equilibrium constant

$$K_p = \frac{p^2_{ClF_3}}{p_{Cl_2F_6}}, \text{ (in atm.)}$$

= 26·9 (9·5°C.), 32·1 (20°C.), 35·4 (24·2°C.) for the reaction $Cl_2F_6 \rightleftharpoons 2\,ClF_3$. The value of Trouton's constant for chlorine trifluoride, 24·1, supported this.[36] From the Raman spectrum, it is concluded that the chlorine trifluoride molecule is probably a symmetrical pyramid,[22] but it has also been stated that the Raman spectrum suggests either an unsymmetrical form or, more probably, association in the liquid state [37] (see page 226).

CHLORINE TRIFLUORIDE: THERMOCHEMISTRY

The heat of the reaction of chlorine trifluoride with sodium chloride was determined by von Wartenberg as 86·8±0·3 kg.-cal., from which

$$\tfrac{1}{3}F_2 + \tfrac{3}{2}Cl_2 \longrightarrow ClF_3 + 28{\cdot}4 \pm 0{\cdot}3 \text{ kg.-cal;}^{38}$$

another value of 76·5 kg.-cal. has been reported for the sodium chloride reaction by Schmitz and Schumacher,[26] but this was only described as a preliminary experiment, and presumably no high order of accuracy was expected. Von Wartenberg found a low vapour density for the chlorine trifluoride used in his work (92·0; calculated for ClF_3 92·6) and, expecially in view of the reported association, this low value is surprising and may indicate the presence of chlorine monofluoride. If such an impurity were present a low result would be obtained, and thus pure chlorine trifluoride should give a higher figure than the 86·8 given above. In view of the recent work of Bode[39] on the formation of active fluorine compounds in the reaction of fluorine with alkali chlorides, it would be reassuring to have some examination of the solid product of the reaction reported. The value obtained for the heat of formation of chlorine trifluoride depends on the difference of the heats of formation of sodium fluoride and sodium chloride, for which Schmitz and Schumacher took their experimental determined value of 39·5 and von Wartenberg took 38·4. The value 38·2 kg.-cal. is, however, obtained if the values for sodium fluoride and chloride in a recent critical review are taken.[20] The values of reaction heats have, therefore, been recalculated to this basis. From von Wartenberg's determination the heat of formation of chlorine trifluoride is 27·8, from that of Schmitz and Schumacher it is 38·1. Correcting the results of the latter workers on the heat of formation of chlorine monofluoride, in the same way, the value of 13·7 kg.-cal, is obtained. From the various values available, a number of values for the heat of reaction of chlorine monofluoride and fluorine can be calculated, as set out in Table V.

TABLE V. - VALUES FOR THE HEAT OF REACTION (kg.-cal.) OF CHLORINE MONOFLUORIDE AND FLUORINE

Qf (ClF) taken as	Heat of (ClF+F_2) taking Qf (ClF_3) as	
	27•8	38•1
11•6	16•2	26•5
12•3	15•5	25•8
13•7	14•1	24•4

CHLORINE TRIFLUORIDE: DISSOCIATION

Further guidance as to the most probable values is given by a study of the equilibrium of chlorine monofluoride and fluorine undertaken by Schmitz and Schumacher who observed the pressure-temperature relation for chlorine trifluoride sealed in nickel and magnesium vessels, measuring the pressure by means of a silica spiral manometer.[40] The nickel vessel was the better, showing very little attack. Their values for the equilibrium constant are:

T, °C	180	200	225	250	300	350
K_p. atm.	0•069	0•212	0•63	2•98	24	143

For the degree of dissociation they give 1•75%, 4•9% and 11•9% at 250°, 300°, and 350°C. respectively.

From the data on the equilibrium constant, the heat of the reaction was estimated to be 25 ± 2 kg.-cal. at 300°C. The work was repeated by Schäfer and Wicke [22] who, using the same technique as in the previous work, obtained results in good agreement. The temperature range was limited, however, owing to attack on the nickel becoming appreciable at 400°C., and although prefluorination at 500 – 600°C. reduced the attack, it did not eliminate it. They therefore used another method, determining the rate of heat loss from an electrically heated nickel filament maintained in an atmosphere of chlorine trifluoride vapour in a silica vessel at ordinary temperature. The dissociation had increased to 50% at 460°C. (±15°). From their results, they found $\log Kp = \frac{5570}{T} + 7{\cdot}06$, and they calculated $\Delta H_0^\circ = 25{\cdot}5 \pm 0{\cdot}5$ kg.-cal., $\Delta H_{298}^\circ = 26{\cdot}5 \pm 0{\cdot}5$ kg.-cal. Referring to the values given in Table V above, there is good independent evidence for the figure 26•5, and it must be concluded that there was a serious error in von Wartenberg's determination. The following figures may therefore be taken:

Heat of formation of chlorine monofluoride	11•6 kg.-cal.
Heat of formation of chlorine trifluoride	38•1 kg.-cal.
Heat of reaction of chlorine monofluoride and fluorine	26•5 kg.-cal.

CHLORINE TRIFLUORIDE: CHEMICAL PROPERTIES

The dissociation of chlorine trifluoride has a bearing on its preparation, which has been considered above, and it has been used as a means of preparing pure fluorine ([41] and see page 17). The exchange between fluorine in chlorine trifluoride, in anhydrous hydrofluoric acid, and in fluorine at ordinary temperatures has been studied[3] by the use of the radioactive isotope ^{18}F. With fluorine, there is no noticeable exchange, whereas with hydrofluoric acid the exchange with liquid chlorine trifluoride is essentially complete in ten minutes

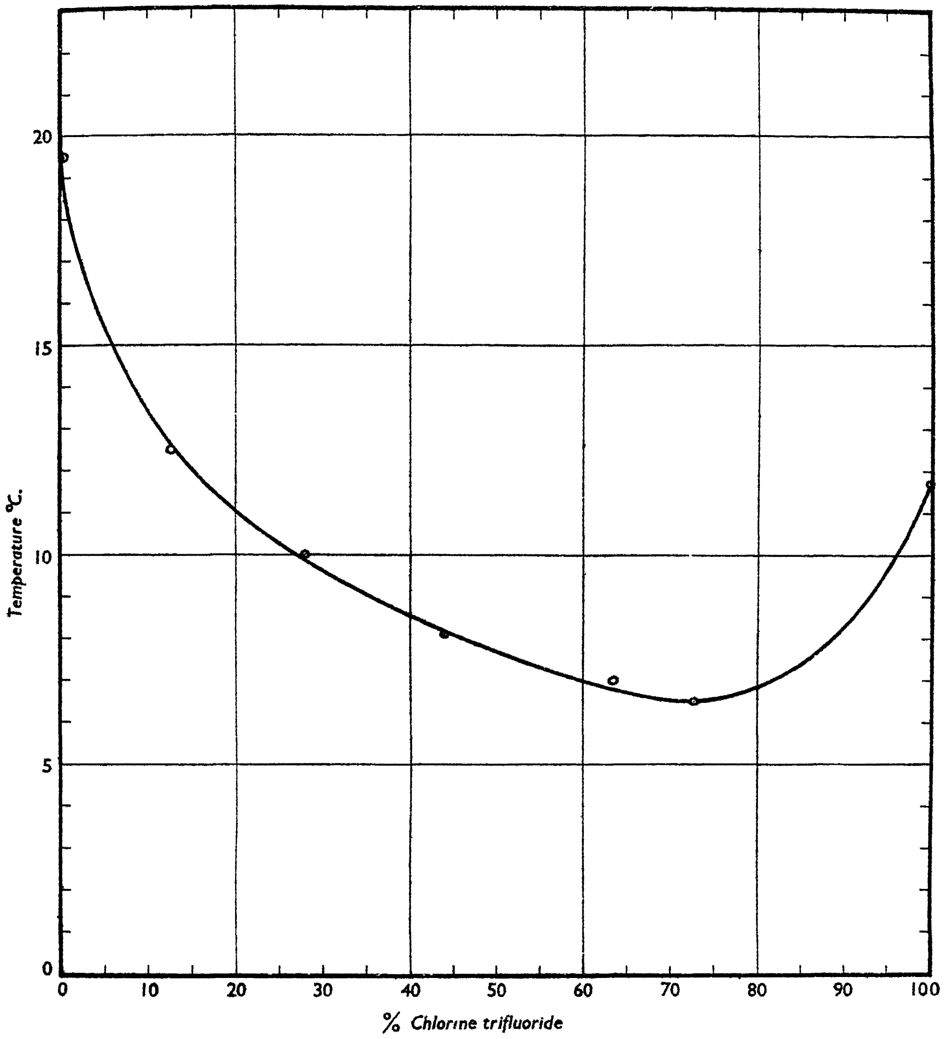

Fig. 1. BOILING POINT - COMPOSITION CURVE

and, with the vapour, in three minutes. It is suggested that with hydrofluoric acid a complex of the type $HClF_4$ is formed, thus facilitating exchange. Chlorine trifluoride and anhydrous hydrofluoric acid are completely miscible[42] and the boiling point curve of the system is shown in Fig. 1.[43] Chlorine trifluoride is soluble in carbon tetrachloride, in perfluoromethyl*cyclo*hexane, and in other halogenated organic compounds which have been obtained by the reaction of chlorine trifluoride with hydrogen-containing compounds.[5,44] One of Ruff's first observations was that chlorine fluoride reacts vigorously with cotton wool and that, other things being equal, burning proceeds more easily in this case than with fluorine itself.[13] In the definitive paper on chlorine trifluoride[19] it is stated that the reaction with benzene, ether, and glacial acetic acid is very violent, sometimes explosive, and with paraffin, vacuum grease, and picein it is also violent; with cloth, cotton wool, paper, and wood there is immediate inflammation; with rubber tubing, violent reaction occurred with gas evolution and the tubing became white and brittle. Reaction with carbon tetrachloride occurred only on warming. There has been very little detailed study of reactions with organic compounds under controlled conditions. It has been stated that, whilst direct and uncontrolled reaction with organic compounds gives rise to carbon tetrafluoride, under controlled conditions both fluorine and chlorine are introduced into the organic molecule.[42] One method of controlling the reaction, which has been the subject of patent claims, is to carry it out in an inert solvent, such as carbon tetrachloride, and examples are given showing that reaction with rubber, paraffin wax, decalin and other organic materials gives rise to products containing about equimolecular amounts of chlorine and fluorine.[6,44] These reactions will occur very rapidly, so that no appreciable concentration of chlorine trifluoride in solution will build up. Should solutions of appreciable concentration be produced accidentally, however, they are liable to be detonated by small amounts of incidental impurity.[43] In another patent the use of a solution of halogen fluoride in anhydrous hydrofluoric acid is claimed; this solution can undergo no further reaction and is therefore quite stable. Examples are given showing the reaction of chlorine trifluoride with hexachlorobutadiene, tetrachloroethylene, trichlorobenzene, kerosene, ligroin, benzene, and benzotrifluoride.[43] In the reaction with benzene in dilute carbon tetrachloride solution, chlorobenzene and fluorobenzene were the main products, together with some addition compounds and condensation products. The reaction was catalyzed, *e.g.*, by cobaltous fluoride.[45] It has been stated that some organic compounds containing nitro-groups, such as T.N.T., hexanitrodiphenyl and its amine, sulphide, sulphone or ether (as well as highly chlorinated compounds), are soluble in chlorine trifluoride but the solutions are extremely sensitive to shock.[43]

Whilst the fuming of chlorine trifluoride in moist air is, presumably, attributable to hydrolysis and the consequent formation of hydrofluoric aci' mist, it is remarkable that no studies on the reaction with water have been published. Ruff observed the formation of silicon tetrafluoride (presumably through a subsequent reaction from the hydrofluoric acid and glass), and of a red liquid solidifying at -70°, which he suggested might be the oxy-fluoride ClOF.[19] The compound has not been isolated and nothing further is known about the course of the reactions. The statement has been made that chlorine trifluoride and water react violently, and that hydrofluoric acid, fluorine oxide, and chlorine are formed.[2] If confirmed this would be surprising; since it implies that the chlorine is more electronegative than the fluorine: it would seem more likely that all the fluorine would go to form hydrofluoric acid, and that the chlorine would give rise to degradation products of chlorous acid. That there is a very violent explosive reaction when chlorine trifluoride and water come together is, however, undoubted. In view of this, the reaction of chlorine trifluoride with other substances may be greatly affected by their state of dryness, as well as by their state of fineness and reactivity, and therefore the following statement by Ruff and Krug, though the most comprehensive, should be taken as a guide only, and not regarded as conclusive,[19] expecially as many of the metals listed must have been in a finely divided state. Potassium, molybdenum, tungsten, iron, rhodium, iridium, osmium reacted with flame; sodium and calcium formed protective crusts but reacted violently on heating; magnesium, aluminium, copper, silver, lead, tin, and zinc showed no reaction at first, but a violent one after starting with carbon. Palladium and platinum showed no reaction. Silicon, red phosphorus, arsenic, antimony, selenium and tellurium inflamed; sulphur also inflamed giving white fumes and a smell of sulphur chloride. Bromine reacted without flame, probably giving bromine trifluoride, and iodine reacted with flame to give a colourless liquid, presumably iodine pentafluoride. Many oxides gave a violent reaction with flame, particularly those of the following metals:- magnesium, calcium, aluminium, lead (dioxide), vanadium and tantalum (pentoxides), chromium (sesquioxide, Cr_2O_3), molybdenum and tungsten (trioxides, MC_3), manganese (dioxide). Oxides of lanthanum, tin (SnO_2), phosphorus (P_2O_5), bismuth (Bi_2O_3) and arsenic (As_2O_3) showed a violent reaction but no flame; chromic acid (CrO_3) gave a violent reaction with brown fumes. No reaction was shown with oxides of zinc, mercury, zirconium, thorium and iron (Fe_2O_3). Quartz gave no reaction, but even completely dry silica- and glass-wool were said to react slowly, and in presence of even traces of moisture were rapidly etched, giving a green gas and a red volatile liquid; occasionally long colourless needles were observed on the surface of the glass. Mercuric iodide, tungsten carbide and glass wool inflamed; potassium iodide and carbonate, silver nitrate, strong sulphuric acid, fuming nitric acid, and 10% caustic soda all gave violent reaction. Explosive reactions occurred with hydrogen, coal gas, sulphur dioxide, hydrogen sulphide and ammonia, and in the last three cases there were white fumes. Graphite and charcoal also burst into flame. It is probable that the reaction with carbon observed above was initiated by impurities. As with fluorine, completely dry and outgassed carbon, charcoal or graphite will not react at ordinary temperatures, but the reaction, *e.g.*, with graphite at 500°C., gives rise to a complex mixture containing (by weight), 29% carbon tetrafluoride, 42% trifluorochloromethane, 7% pentafluorochloroethane, and derivatives of propane and higher compounds.[46] Among carbon compounds, carbon monoxide and chlorine trifluoride, diluted with two volumes of nitrogen, when passed over active charcoal at -18° gave a 10% yield of carbonyl chlorofluoride.[28] Similarly cyanogen gave a mixture of fluorocarbon-nitrogen compounds and difluorobromonitromethane gave fluoropicrin.[47] Whilst the earlier work on chlorine trifluoride indicated that it attacked glass, later studies showed that if water adsorbed on the glass is removed by baking and hydrofluoric acid is eliminated from the chlorine trifluoride by sodium fluoride treatment, the attack on glass is prevented. Thus the work on the density of the liquid was carried out in Pyrex glass, without any signs of etching.[34] American workers have used tubes of 'Fluorothene', a polymer of trifluorochloroethylene, as being completely resistant to attack; thus work on the spectrum was carried out in this material[37] using windows of potassium bromide or sodium chloride. On the other hand these halides readily react with chlorine trifluoride on gentle warming, and the reaction with sodium chloride was used in the thermochemical work described above. Of course in this case the solid would be in a granular or powder form.

The state of subdivision naturally influences profoundly the reaction observed. Thus Ruff reported many metals above as reacting, whereas in the massive form and at normal temperatures many of these would be regarded as completely resistant. This is paralleled by the resistance of metals to oxygen in massive form, although when sufficiently finely divided they may, as in the case of iron, be pyrophoric. The resistance of metals to chlorine trifluoride is very similar to their resistance to fluorine. Thus for storing chlorine trifluoride, vessels made of iron, nickel, cobalt or their alloys have been claimed in a patent of German origin,[48] which cites particularly, among the alloys, the stainless steel V2A. Whilst this alloy and chromium metal are unaffected, many metals have been fluorinated in autoclaves made of V2A, – mercury, silver, copper, titanium, cobalt, platinum and lead.[47] Chlorine trifluoride is contained, in the liquid form, in mild steel cylinders. The ready availability of chlorine trifluoride and its relatively easy handling afford a convenient way

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of making higher fluorides, such as cobalt trifluoride or silver difluoride, in the laboratory.[6] This intermediate treatment for organic fluorination may be necessary since, as noted above, the direct reaction of chlorine trifluoride with organic compounds under controlled conditions leads to the introduction of both chlorine and fluorine into the organic molecule.

It is generally assumed that massive metals are protected from attack by the formation of closely adherent fluoride films and as many fluorides are involatile this is probably a reasonable assumption. When the metal forms a relatively volatile fluoride, as in the case of tantalum, there is no protection, and this applies to platinum at slightly elevated temperatures. In certain cases chlorine trifluoride causes much greater corrosion than fluorine alone; Ruff and Giese noted the resistance of copper to fluorine, even when finely divided and at 350°C.,[29] but the addition of a little chlorine to the fluorine greatly accelerated the attack on the metal. Thus, whilst copper is a very good metal to use with fluorine, it is not so good with chlorine trifluoride. Bromine trifluoride, as will be seen below, forms complex salts of the form $KBrF_4$. No such complexes have been isolated in the case of chlorine trifluoride although Emeléus has said that chlorine trifluoride is absorbed by potassium fluoride but without the formation of stable compounds.[5] Some mention should be made of the reported preparation of a fluorochloride derived from a hypothetical chlorine pentafluoride. The salt was made by reaction of strong aqueous hydrofluoric acid with potassium chlorate, and was assigned the formula $KClF_6,KF$.[49] Emeléus and Sharpe suggest that it is most unlikely that any halogen fluoride derivative would exist in the presence of water or of 40% hydrofluoric acid, and that the product must have been a mixture of potassium chlorate and potassium acid fluoride.[50] Chlorine trifluoride has not yet found any regular uses, and the reasons for which the German 1000-ton plant was erected are obscure. Obviously a chlorine trifluoride-hydrogen flame will reach very high temperatures, and its use for cutting and welding copper has been described.[51] Owing to the ease of handling and its high fluorine content, chlorine trifluoride may readily offer a source of high energy yields on reaction with hydrocarbons, and it has been mentioned as a possible constituent of rocket fuel.[52] An interesting and practical use in the laboratory has been described.[53] The oxygen from samples of silicate rocks was liberated by heating with chlorine trifluoride and anhydrous hydrofluoric acid for 20 hours at 430°C. and the oxygen was then analysed for its isotopic constitution. Ruff and Krug[19] described an analytical method for chlorine trifluoride. The liquid was filled into a silica bulb with a long capillary outlet. This was weighed, and immersed in 10% caustic soda, and then by gentle shaking the capillary was broken and absorption proceeded steadily, though if the bulb itself was broken there was a violent explosion. The solution was then analysed in a standard manner. It is said that if the bulbs were of glass, they were destroyed in a few minutes, but in the light of later results this can only indicate the presence of impurities, probably a good deal of hydrofluoric acid.

BROMINE MONOFLUORIDE

Ruff and Menzel suspected the formation of a lower fluoride than bromine trifluoride from the low density (mol.wt. = 108·5) of the first fractions evolved from a crude pentafluoride preparation.[54] The definitive paper by Ruff and Braida[55] is, however, unsatisfactory. Thus in a review of the halogen fluorides it has been said:[1] 'Based on analysis, density, and vapour pressure data, the conclusion was reached by Ruff and Braida that the mixture condensed in one of the -120°C. traps contained almost 50% of bromine monofluoride. The present reviewers do not find the evidence altogether convincing'. This criticism seems well justified. The compound was not obtained in a pure state, as it decomposes into the higher fluorides and bromine. No analyses could therefore be given, and the formula BrF was proposed for this suspected lower fluoride by analogy with chlorine monofluoride and the odd number of fluorine atoms in all the known halogen fluorides. Bromine and fluorine combine rapidly at room temperature, with much evolution of heat, when brought together in a copper T-piece. If the reaction product is condensed in a silica vessel, cooled at the bottom to -150°C., there condenses in the lowest, coldest, part the most volatile bromine monofluoride, in the form of shiny orange-red plates, with a colour reminiscent of bichromates. Above this condensate are compact, dark red crystals of bromine, and higher again the pale greenish needles of bromine trifluoride, with in between some finely distributed pentafluoride and also, finally, some silicon tetrafluoride. This is really the most positive observation recorded. For the production from bromine and fluorine, an all silica apparatus is described. The bromine, carried as vapour in a stream of nitrogen, mixes with fluorine in a T-piece immersed in water and held at 10°C. The reaction of bromine and fluorine is very temperature-sensitive; the velocity is very small at 0°, whilst at 50 – 60° there is no monofluoride in the bromine tri- and pentafluoride. It is essential that in the reaction-T, the walls should be smooth, or the yield of monofluoride is bad. Copper may be used, but with platinum practically no monofluoride is obtained. Below the reaction-T is a trap kept at +10°, and then a series of traps at -20°, -50° and -120°, and finally one in liquid air. The analyses of the contents of the traps give ratios F:Br of 2·75, 3·3, 2·70, 3·62, 2·48: molecular weights from vapour densities are 129·3, 145·4, 134·9, 153·7 ($BrF = 99$; $BrF_3 = 137$; $BrF_5 = 175$). Some calculations made show contents of from 18·5 to 49·3% of bromine monofluoride, with bromine and the tri- and pentafluorides, and in some cases silicon tetrafluoride and oxygen. It is suggested that bromine also reacts with the tri- and pentafluorides to give the monofluoride, but that as the reactions are reversible the pure monofluoride cannot be isolated. Some evidence is offered for a melting point about -33°C., and for a vapour pressure equation

$$\log_{10} p = 7{\cdot}2798 - \frac{1303{\cdot}4}{T},$$

giving a boiling point of +23°C. This evidence, however, is slight, confused, and dubious. If Ruff and Braida had a lower fluoride, the evidence provided gives little definite information regarding its composition and properties.

In a study of the absorption spectrum of bromine trifluoride by other workers about the same time,[56] it was said 'In one experiment in which bromine was present as well as bromine trifluoride, it was found on heating the tube to about 70°C. that the absorption due to bromine trifluoride diminished and a new band appeared. The original spectrum reappeared on cooling. Bromine monofluoride is known to be formed under these conditions, and it would appear to be likely that the new band is due to this compound'. This, however, is contrary to Ruff and Krug's observation that low temperatures favoured formation of the monofluoride. The band spectrum of bromine monofluoride has been studied, and it was found necessary to study the conditions of existence of the different bromine fluorides. As bromine interferes even in small quantities, owing to its intense absorption in the visible region, it is desirable to work with bromine absent. Owing to the equilibrium $3BrF \rightleftharpoons BrF_3 + Br_2$, a considerable excess of fluorine must be used. In these conditions, a mixture of gases containing considerable quantities of bromine mono- and trifluorides is obtained, with little pentafluoride and practically no bromine or fluorine.[58] No further information or experimental details are given, but the authors state that whilst the tri- and pentafluorides are colourless, the monofluoride has a pale yellow colour. In another contribution by the same authors it is said that, in suitable circumstances, the reaction $Br_2 + F_2 \rightarrow 2BrF$ gives rise to a flame and strong heat evolution, so that it must be strongly exothermic. From the spectrum, the heat of dissociation of BrF to atoms must be of the order of 50 kg.-cal. and the heat of formation from the elements must be exothermic to the extent of approximately 20 kg.-cal.[57] It has also been suggested that six lines observed in the absorption spectrum of bromine tri- and pentafluoride are to be attributed to the monofluoride, and these lines become more intense when bromine vapour and fluorine are admitted at about equal pressures into the absorption cell.[58a]

BROMINE TRIFLUORIDE

After the simultaneous characterization of this compound by Lebeau and by Prideaux in 1905, it was not further studied until Ruff reinvestigated it about 1930. There has been an increasing interest in bromine trifluoride since that time, and it has now become an article of commerce, workers referring to its being available in steel cylinders.[3] In the preparation, in some cases Lebeau's method has been used, viz. bubbling gaseous fluorine into liquid bromine, although as an aid to purity the fluorine was liquefied and fractionally distilled before the reaction,[56] and the bromine trifluoride produced was fractionally distilled in a stream of fluorine in a Pyrex apparatus. This method was also used in the most recent description.[59] In his classical work on fluorine, however, Ruff described a modified method which has been preferred by most workers.[9] Bromine vapour, carried in a stream of nitrogen, is mixed with the fluorine in a small T-piece of platinum, the nitrogen flow bubbling through liquid bromine and being so adjusted in relation to the fluorine that the gas leaving the platinum tube has a minimum of colour; the gases are then cooled to condense the bromine trifluoride. This method, which is further described in a later paper, has been used by a number of workers. In the later paper of Ruff and Braida a copper T-piece replaced that of platinum, the product was condensed out in a silica trap, and excess fluorine was used, which was condensed out in a trap cooled in liquid air.[60] The method has been used by Emeléus and his school, but a water-cooled copper trap follows the copper T[61] and in addition to the Ruff and Braida method, the method of Kwasnik (see below) is also referred to.[62] In Kwasnik's method reaction is carried out in an iron apparatus, at 80 – 100°C., without any diluent: 10% excess fluorine is used, and there is a 90% yield of bromine trifluoride, of 98% purity.[28] In another method, liquid bromine is fed into the upper end of a slightly inclined water-cooled copper tube, which is supplied with fluorine at the lower end. The cooling is adjusted to keep the temperature between 15° and 50°C., and liquid bromine trifluoride is withdrawn at the lower end of the reactor.[2] It has already been seen above that Ruff and Krug described the reaction of bromine and chlorine trifluoride, and this also may be regarded as a method of preparing bromine trifluoride.

It has been usual to subject the crude bromine trifluoride to distillation, but information on the content of impurities before and after this treatment is noticeably lacking. In one case only was it found, by a cryoscopic method, that the content of impurities was 0·09 mole per cent.[59] It is obvious that hydrogen fluoride present in the fluorine will appear in the bromine trifluoride, and moisture from the bromine, or from other sources, will also produce hydrogen fluoride. The bromine may also introduce chlorine. Any exposure to moisture after production will lead to contamination with hydrogen fluoride and undefined hydrolysis products, – bromine, bromine oxyfluorides, etc. It may be expected that the bromine to fluorine ratio in production will have a profound influence on composition, leading on the one side to contamination with the monofluoride, on the other side to pentafluoride. The extent to which any of these contaminants may form complexes or azeotropes being unknown, distillation is not a completely satisfactory guide to purity. Ruff and Braida, who handled their product in silica, said that attack on silica was noticeable at 30°, so that they purified it by distillation in silica in vacuo at 20°C.[60] But to what extent the attack on the silica may have been due to traces of hydrogen fluoride or to other contamination is not known. White and Goodeve, as noted above, used purified fluorine and dry bromine, and were able to distil the product in Pyrex glass,[56] although Ruff always said that glass could not be used owing to the rapidity of attack. But in carrying out this distillation, as they did, in an atmosphere of fluorine, it might be expected that bromine pentafluoride would be formed. Sharpe and Emeléus distilled the trifluoride from a steel retort, collecting the fraction of b.p. 126° – 128° in steel bottles with screw-on steel caps.[61] As a small amount of ferric fluoride was formed in these storage containers, the material was redistilled immediately before use in silica apparatus, at room temperature and reduced pressure. It is said that all the possible impurities – bromine, hydrogen fluoride, bromine monofluoride and the pentafluoride – were more volatile than the trifluoride, and that the change in colour of the liquid from orange to light yellow, owing to the removal of the least volatile impurity, bromine, affords a convenient visual indication of when to begin collecting the pure trifluoride.[35] In another case the pure bromine trifluoride was distilled from a copper vessel.[63] Oliver and Grisard, who introduced the cryoscopic method as a guide to purity, distilled under 27 in. vacuum through a nickel column.[59] Rogers and Katz, using commercial material in steel cylinders, merely say that it was purified by distillation.[3] The variety of materials available for handling bromine trifluoride is seen from the above account. Silica is very generally preferred, although Pyrex glass has been used. Of the metals, iron is generally used as the container for commercial handling; there is a suggestion that small quantities of ferric fluoride are formed, but it seems likely that this may arise from scale and rust present on the surface. Copper is used, but the warning about corrosion at high temperatures should be noted here, as with chlorine trifluoride, and in one case nickel was used in preference to copper, because the latter is more readily attacked by free bromine.[59] Nickel is here, as generally in the fluorine field, probably the best metal to use: it will be seen below that objections can be raised to using gold or platinum. The use of containers of iron, nickel, cobalt or their alloys, especially V2A stainless steel, for bromine trifluoride or for chlorine trifluoride has been patented.[48]

BROMINE TRIFLUORIDE: PHYSICAL PROPERTIES

Liquid bromine trifluoride in its purest form has a pale straw colour. By slight access of moisture or attack on glass, it deepens in colour, and may become quite red. This is presumably due to hydrolysis, the instability of the bromine oxides leading to the liberation of free bromine, but there is no experimental information. Ruff and Braida report that crystallization from the liquid produces shiny needles up to 20 mm. long and 1 mm. thick whilst condensation from the vapour occasionally gives also prisms 2–3 mm. diameter, and they suggest that there may be two different forms of the solid.[64] The purest liquid gives white crystals. Their value for the m.p., 8·8°, was appreciably higher than had previously been given,[60] and a more recent determination gives the true m.p. of pure bromine trifluoride as 8·77°.

The vapour pressure was measured by Ruff and Braida.[64] For values up to 20°C., a silica apparatus with a quartz spiral manometer was used; the results may have been affected by a gradual attack on the silica and formation of volatile products, or of substances soluble in the liquid and lowering its vapour pressure. From 20° to the b.p., the Smith-Menzies method was used in a platinum vessel with sulphuric acid as the sealing liquid. Though this underwent reaction with formation of volatile products, it was the best of all the liquids available. The vapour pressure curve obtained was

$$\log p = 8{\cdot}41954 - \frac{2220{\cdot}2}{T} : \text{ b.p. } 127^\circ \pm 1;$$

latent heat of evaporation, 10 kg.-cal./mol.; Trouton's constant, 25·3; critical temperature (estimated), 327°C. The vapour pressure was also determined by Oliver and Grisard between 17 and 1808 mm. (39 – 155°C.) in a nickel apparatus connected to a mercury manometer by helium-filled lines, on a sample containing 0·09 mole per cent of impurity.[59] The results were expressed in the equation:-

$$\log_{10} p_{mm} = 7{\cdot}74853 - \frac{1685{\cdot}8}{t + 220{\cdot}57}$$

to within less than 1 mm., up to 155°C. (1808 mm.). Some decomposition occurred in the apparatus, and 'after an unsuccessful attempt to measure the pressure at 165°C., it was discovered that most of the 60 g. sample had decomposed and diffused into an adjacent liquid nitrogen cold trap.' This equation gives a normal b.p. of 125·76°C., appreciably lower than the value of Ruff and Braida, and actually outside the range of distillation over which pure material has been collected by some workers.[61] The equation

$$\Delta H_v = 7714 \left[\frac{t + 273{\cdot}16}{t + 220{\cdot}57}\right]^2$$

is given for the latent heat of fusion in g.-cal./mole, from which at the normal b.p. ΔH_v = 10·244 kg.-cal./mole, based on the vapour pressure equation given above and the Clapeyron-Clausius equation.[59] These workers also determined the latent heat of fusion, 2874·6 ± 3·0 g.-cal./mole, and the specific heat between 14°K. and 320°K. Some of the results are given in Table VI.

TABLE VI. - MOLAL HEAT CAPACITIES, BROMINE TRIFLUORIDE[59]

	Solid										Liquid	
Temp. °K.	14	30	50	70	90	110	150	200	250	281·93	281·93	320
$C_{\text{satd.}}$, g.-cal./deg	1·03	4·28	7·54	10·00	12·08	13·76	16·69	19·42	21·72	23·32	29·59	30·04

The entropy values derived from these determinations are given in Table VII.

TABLE VII. - ENTROPY OF BROMINE TRIFLUORIDE IN g.-cal./deg./mole[59]

$S_{14^\circ\text{K.}}$ Debye, 3° freedom, (θ = 115·58)	0·357
$S_{14-281{\cdot}93^\circ}$ Solid, graphical	30·359
S_{fusion} 2874·7/281·93	10·197
$S_{281{\cdot}93-298{\cdot}16^\circ}$ Liquid, graphical	1·660
Entropy of liquid at 298·16°K.	42·57 ± 0·10
$S_{\text{vaporization}}$ (11,370/298·16)	38·14
$S_{\text{compression}}$ (R ln 7·65/760)	–9·14
Entropy of ideal gas at 298·16°K. and 1 atm.	71·57

The density of the solid was given, very approximately, by Ruff and Braida as 3·23 g./cc., that of the liquid by the equation $d = 3{\cdot}623 - 0{\cdot}00277\ T$ (°K.): the density of the liquid at the m.p. was 2·843 g./cc. The electrical conductivity of the liquid was measured between platinum electrodes in a silica apparatus.[55] On two samples, A and B, described merely as carefully purified, the results of Table VIII were obtained.

TABLE VIII. - ELECTRICAL CONDUCTIVITY OF LIQUID BROMINE TRIFLUORIDE[35]

Temperature, °C	10·1	14·8	25·0	35·0	45·0	55·0	
cond. $F \times 10^3$, ohm^{-1}cm.$^{-1}$ (A)	8·12	8·11	8·00	7·78	7·48	7·08	
Temperature, °C.	9·0	10·0	20·0	30·0	40·0	50·0	60·8
cond. $F \times 10^3$, ohm^{-1}cm.$^{-1}$ (B)	8·13	8·14	8·09	7·87	7·58	7·19	6·75

After the determination at 60° on sample B, a redetermination of the value at 20°C. reproduced the original value. The value also changed little with time, but addition of free bromine caused a decrease in conductivity. The conductivity of the solid was much less than that of the liquid, and showed a positive temperature effect, increasing from $2{\cdot}36 \times 10^{-5}$ at 4° to $17{\cdot}35 \times 10^{-5}$ at 8°. On applying a direct current, there was no observable decomposition voltage; the liquid followed Ohm's low from quite low voltages (<1·0 volt). No gas evolution occurred, but in the neighbourhood of the cathode a brown colour developed while around the anode the light yellow colour of the liquid disappeared, and there was a sharp demarcation between the brown and the yellow liquid. It has been suggested that these colour changes are associated with the formation of bromine monofluoride and pentafluoride from the ions discharged at the cathode and anode, BrF_2 and BrF_4 respectively:

$$2BrF_2 \rightarrow BrF + BrF_3 : 2BrF_4 \rightarrow BrF_5 + BrF_3.$$

The conductivity of liquid bromine trifluoride is much higher than that of chlorine trifluoride (<10^{-6} ohm^{-1}cm.$^{-1}$) or iodine pentafluoride ($1{\cdot}6 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$ at 10°C.) and this difference is further considered below.

Bromine trifluoride is miscible in all proportions with anhydrous hydrofluoric acid[43] but is only partially miscible with bromine.[57] From the value of Trouton's constant for bromine trifluoride, 25·3 compared with 23·2 for bromine and 23·7 for the pentafluoride, Ruff and Braida considered there was possibly some association in the liquid.[64] Radioactive tracer studies with ^{18}F show that rapid exchange occurs between the fluorine of hydrogen fluoride and bromine trifluoride in the liquid phase, and it is considered that this indicates the formation of intermediate complexes.[3]

BROMINE TRIFLUORIDE: CHEMICAL PROPERTIES

Ruff made a considerable number of qualitative observations on the reactions of those halogen fluorides which he had discovered, but bromine trifluoride was not one of these. The reactions of bromine trifluoride will be very similar, in many respects, to those given by Ruff and Krug above for chlorine trifluoride, but a cautionary note was given there with regard to the reliability of the information, and we cannot do better than quote here the words of Booth and Pinkston.[2] 'To some extent, the halogen fluorides appear to react with all metals. In some cases, at low or intermediate temperatures, a protective fluoride film is formed on the metal surface which halts further action. This fact permits chlorine trifluoride, bromine trifluoride, bromine pentafluoride and probably the other four members of the group to be handled in mild steel up to about 250°C. in copper up to about 400°C.* and in nickel up to about 750°C.

Where no protective film is formed, the reaction is vigorous. This is especially true where volatile metal fluorides, such as molybdenum hexafluoride and tungsten hexafluoride, can be formed. Unfortunately, almost no satisfying information on the behaviour of metals falling between those extremes is available. Statements have been made that certain of the metals ignited at room temperature whereas others required warming; but the surface cleanliness, in some cases the degree of sub-division, and often the effective temperature at which reaction started were not clearly defined. Almost no information on the reaction products has been reported.'

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* It has been remarked under chlorine trifluoride (see page 158) that this limit for copper is open to doubt; it should probably be much lower, perhaps 300°C.

There was little interest in bromine trifluoride prior to 1940 apart from the determinations of physical properties by Ruff and Braida and a solitary patent describing the reaction with carbon tetrachloride (see page 167). Thereafter, however, McBee et al. took an interest in bromine trifluoride as an organic fluorinating agent in a particular field which will be reviewed below, and there was a particularly interesting development of the field of bromine trifluoride reactions by Emeléus and his school. Analogously with chlorine trifluoride, but with the qualifications indicated by Booth and Pinkston, bromine trifluoride will react with many substances, forming fluorides and liberating bromine. But another factor also enters in – the solubility of fluorides in bromine trifluoride – and this leads to a very interesting field of chemistry. Reaction will occur not only with elements, but also with halides, oxides, and oxysalts, and as bromine trifluoride is an ionizing solvent the fluorides immediately formed may behave as acids or bases in this solvent. When appropriate oxysalts, or mixtures of materials, react, neutralization reactions may occur with the formation of complex fluorides and this has led to useful preparative methods for many new complex fluorides.

No studies of the reaction with water have been published; it is said that hydrofluoric, bromic and hypobromous acids are formed[2] and that the complex which bromine trifluoride forms with potassium fluoride yields with water bromine, bromic acid, hydrofluoric acid and oxygen.[61] The reactions studied by Emeléus and his school, which will now be considered in detail, were carried out in silica vessels, the bromine trifluoride, as noted above, having been finally distilled in silica under reduced pressure. There is, however, some slight reaction with silica, which may be enhanced in certain circumstances (see below). The reaction of a number of metals has been described. Platinum does not react at temperatures up to the boiling point, but is attacked by the potassium fluoride–bromine trifluoride complex at 280° giving the tetrafluoride.[61] Auric fluoride is soluble in bromine trifluoride, and hence this solvent dissolves the metal.[65] Silver is attacked also, because of the formation of a soluble salt, and in several cases the reaction of bromine trifluoride with mixtures containing metallic silver has been used to prepare complex fluorides of silver.[66-69] Niobium and tantalum react with incandescence, and a technique to control the reaction was described.[66] The powdered metals were suspended in liquid bromine, the mixture cooled in liquid air, and bromine trifluoride slowly dripped on the cold mass. Titanium[67] and molybdenum and vanadium[69] as powders also react with incandescence, and tin[70] reacts violently,

Halides other than fluorides are generally attacked by bromine trifluoride, giving rise to fluorides, usually in the highest valency state. The fluorides may be soluble, as exemplified by the fluorides of sodium, potassium, rubidium and caesium and of silver (AgF) and barium; and by auric fluoride, stannic fluoride, platinic fluoride, rhodium tetrafluoride, and the pentafluorides of arsenic, antimony and bismuth (slight), niobium and tantalum. Other fluorides show no appreciable solubility. Lower fluorides are usually fluorinated to the higher state, *e.g.*, antimony trifluoride reacts gently with evolution of bromine,[70] but argentous fluoride is an exception, dissolving without reaction. The rate of attack of bromine trifluoride on chlorides, bromides and iodides varies, possibly owing to variation in the solubility of the fluoride produced. Thus potassium and sodium chloride, bromide and iodide are rapidly attacked, and whilst chlorine and bromine seem to be evolved in the elementary state,

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the iodides seem to give iodine pentafluoride.[61] The chlorides of silver, lithium and cadmium are rapidly attacked, as also are those of barium, sodium, calcium, cæsium and rubidium. With aluminium and ferric chlorides the conversion to fluorides is slow. Lower chlorides of elements of variable valency are converted, but not completely, to fluorides of higher valency: cuprous chloride gave a product analysing as 70% CuF_2; thallous chloride a product analysing as 80 – 90% TlF_3; plumbous fluoride, chlorine and bromide gave products containing 20% PbF_4; cobaltous chloride gave almost solely cobaltic fluoride; uranium tetrafluoride was quantitatively converted to the volatile hexafluoride. Stannous chloride inflames with liquid bromine trifluoride, the product being stannic fluoride with varying quantities of retained bromine trifluoride.[70] Platinum tetrachloride and tetrabromide are vigorously attacked, giving, with excess of bromine trifluoride, a red solution; rhodium tetrabromide behaves similarly; palladium bromide gives a brown product.[71] Auric chloride is attacked and the product is dissolved by excess of the reagent.[65] Vanadium trichloride is converted to the pentafluoride, and molybdenum dibromide is converted to the volatile hexafluoride.[69] The treatment of phosphorus pentabromide to give the pentafluoride has been carried out in admixture with other materials to give hexafluorophosphate complex salts;[68] the pentachloride behaves similarly[72] and an interesting case is the use of nitrosyl chloride in a similar manner to give complex salts. This method, the treatment of mixtures with bromine trifluoride, has been used with many of the halides referred to above, and will be dealt with below when considering bromine trifluoride as a solvent. Finally, mention should be made of the reaction with nitrosyl tetrachlorobismuthate and nitrosyl hexachlorostannate to give complex fluorides.[67] It is not surprising that ammonium halides react explosively with bromine trifluoride.[61]

The reaction of bromine trifluoride with many oxides has also been described. Of particular interest is a report on the reaction with uranium oxides, the first of a valuable series from the Cambridge school. A rapid and quantitative reaction occurs, below the boiling point, with UO_2, U_3O_8, and UO_3, and the uranium is completely volatilized as the hexafluoride.[73] In a further paper, the behaviour of many oxides is reported.[72] At the same time it is suggested that Ruff over-emphasized the activity of bromine trifluoride, as in many cases the oxygen evolution was not complete. The simple apparatus in which the reactions with oxides were carried out is described (Fig. 2; p. 166). Freshly distilled bromine trifluoride in A was cooled in liquid air, a weighed amount of oxide was placed in C and the apparatus pumped out and filled with nitrogen; C and traps D and E were cooled in liquid air, then A was allowed to warm up and by rotating about joint B, bromine trifluoride slowly dripped into the oxide, which was initially cooled in liquid air. Finally C was warmed up to room temperature, and in some cases the bromine trifluoride was refluxed for two hours. After reaction, bromine trifluoride was evaporated off to trap D, and the weight of this, and the contents of C, determined, whilst the volume of oxygen was also measured. The whole of this work is notable for its precise quantitative character and for the quality of the supporting analytical data. The oxides of copper (CuO), bismuth (Bi_2O_3), thallium (Tl_2O_3), silicon, germanium, titanium, selenium (all XO_2), arsenic and antimony (X_2O_3), uranium (UO_3), and iodine (I_2O_5) all gave quantitative evolution of oxygen, the product being the higher fluoride (except IF_5) and, in the case of antimony, with one mol. of additional bromine trifluoride. The oxides of beryllium, magnesium, zinc, cadmium, mercury, calcium, aluminium, cerium (CeO_2), tin (SnO_2), lead (PbO and PbO_2), zirconium, thorium, manganese (MnO_2) and iron (Fe_2O_3) reacted incompletely, the product being a mixture of fluoride and oxide. Vanadium pentoxide gave VOF_3, bismuth oxychloride gave BiF_5. It is again remarked that the removal of oxygen from vanadium pentoxide was slow.[74] Niobium and tantalum pent-

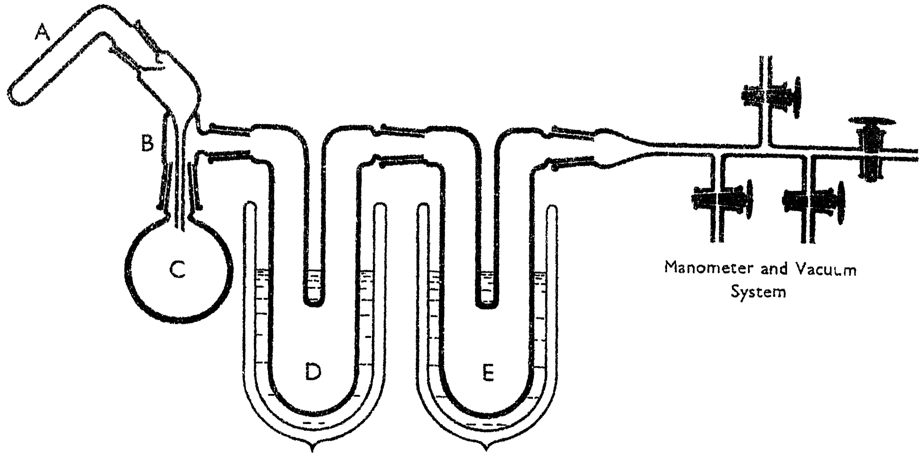

Fig. 2. APPARATUS FOR THE REACTION OF BROMINE TRIFLUORIDE WITH OXIDES AND OXY-ACID SALTS

oxides reacted vigorously to give a clear solution, from which a complex of the fluoride with bromine trifluoride was recovered on evaporation.[66] Bismuth pentoxide also reacted vigorously, the initial products containing the oxyfluoride, trifluoride, and trioxide, but giving finally a solution of a complex of the pentafluoride.[66] The reaction of antimonious oxide with bromine trifluoride was violent and was moderated by using bromine as a diluent; the product, $SbBrF_8$, was soluble in excess of the reagent. Antimonyl chloride reacted even more violently than the oxide, to give the same product.[70] The reaction of some oxides in presence of nitrosyl chloride to give complex fluorides of the nitrosyl ion has been described.[67] Thus boric oxide in these circumstances gave nitrosyl fluoborate, $NO.BF_4$.

The reactions of germanium dioxide, silica, arsenic and antimony have also been described. Sulphur trioxide dissolved in bromine trifluoride without any evolution of oxygen; on evaporation a sticky white solid was obtained, hardly fuming in moist air, and it appeared that complex formation occurred. Some reactions of dinitrogen tetroxide have been described, and are considered below.[68] The reaction of cobalt oxides with bromine trifluoride and other halogen fluorides has been mentioned by other workers,[2] and the reaction of carbon monoxide has been referred to.[28] When this gas was passed in a slow stream through bromine trifluoride in a cooled iron vessel between 8° and 30°, quantitative yields of carbonyl fluoride and carbonyl fluorobromide were obtained. At rather high temperatures, explosions occurred. Thionyl chloride with bromine trifluoride gave thionyl chlorofluoride $SOClF$; and when sulphur dioxide, bromine and bromine trifluoride were shaken together in an autoclave at room temperature for several days the product was sulphonyl bromofluoride SO_2BrF.[28]

The reaction of oxy-salts with bromine trifluoride has been used to give complex fluorides; e.g., potassium metaphosphate gave the hexafluorophosphate KPF_6,[68,72] and these general reactions will be considered in a later paragraph in which the behaviour of nitrates, sulphur oxyacids, and other compounds is discussed. But in certain cases this may not, or cannot, occur

Thus many iodates gave the metal fluoride (and, apparently, though this was not specified, iodine pentafluoride) with evolution of all their oxygen.[72] Potassium bromate gave a 100% yield of oxygen with the formation of the bromine trifluoride complex; potassium chlorate gave only one third of its oxygen, possibly because chlorine dioxide or the chlorine oxyfluoride ClO_2F is formed.[72] Carbonates also were decomposed but only one third of the oxygen was recovered as such; and if carbon dioxide was evolved this was not reported.[72]

Though chlorine trifluoride does not normally react with carbon tetrachloride, bromine trifluoride reacts immediately with this compound, and this has been patented as a process for making fluorochloromethanes.[75] Carbon tetrachloride dripped into cold bromine trifluoride reacted immediately, and difluorodichloromethane, trifluoromonochloromethane and tetrafluoromethane were found in the gas evolved. The same result can be achieved by bubbling fluorine into a solution of bromine in carbon tetrachloride. The reaction has been studied by Emeléus et al.,[63] who found that in carrying it out at atmospheric pressure the escape of the partially fluorinated materials limited the formation of the more highly fluorinated and more volatile products, so that trichlorofluoro- and dichlorodifluoromethane were the principal products. Reaction occurred immediately as bromine trifluoride dripped into the carbon tetrachloride. By carrying out the reaction in an autoclave, the bromine trifluoride being introduced in a separate container, so that the reactants did not mix until the autoclave was sealed, there was a greater production of the trifluoro- derivative. Carbon tetrabromide, a solid, in solution in bromine, gave mainly monofluorotribromomethane, but by dripping bromine trifluoride on to the solid a yield of 94% of trifluorobromomethane was obtained. Inflammation occurred when bromine trifluoride dripped on to cooled carbon tetraiodide; no formation of iodofluoromethanes was observed, but difluorodibromomethane and carbon tetrafluoride were detected. The reaction of bromine trifluoride with hexachlorobenzene led to saturation of the double bonds and some substitution of the chlorine, a product with average composition corresponding to $C_6Br_2Cl_4F_6$ being obtained.[76] The reaction was carried out in a nickel pot with a stirrer, hexachlorobenzene being added in small portions to bromine trifluoride already in the pot, at 0°C. By treating this product with antimony pentafluoride the proportion of fluorine was increased, and by dehalogenation with zinc a series of fluorochloro-benzenes, -*cyclo*hexenes and -*cyclo*hexadienes was obtained, including some hexafluorobenzene. A similar series of compounds was obtained from pentachlorobenzotrifluoride, including some octafluorotoluene.[76] These preparations, extensively studied by McBee, Lindgren and Ligett, have been the subject of a series of patents for the treatment with bromine trifluoride of the chlorocarbon derivatives of toluene, xylene, mesitylene, naphthalene and heptane[77] and of diphenyl,[78] and for the compounds obtained by the procedure referred to above, which are derivatives of benzene and the other hydrocarbons named.[79-84]

BROMINE TRIFLUORIDE AS A SOLVENT

It has already been noted that in a number of cases the fluorides produced by the action of bromine trifluoride on other compounds are soluble in excess of the reagent. On evaporating the solution, complexes containing bromine trifluoride are obtained, and even when the fluoride is not noticeably soluble, it may still be obtained as a complex. Thus the fluorides of potassium, silver and barium are soluble, and from the solutions can be obtained KF,BrF_3, AgF,BrF_3 and $BaF_2,(BrF_3)_2$ respectively. Sodium fluoride is soluble and though the complex more readily loses bromine trifluoride in vacuo, NaF,BrF_3 has been prepared. The fluorides of rubidium, cæsium, calcium and strontium retained some bromine trifluoride, but the products were of ill-defined composition.[61] Antimony pentafluoride, stannic fluoride,[70] auric fluoride,[68] platinic fluoride,[71] niobium, tantalum, and bismuth pentafluorides,[66] and arsenic pentafluoride,[72] were all soluble and gave products which analysed respectively as SbF_5,BrF_3, $SnF_4,2BrF_3$, AuF_3,BrF_3, PtF_4,BrF_3, NbF_5,BrF_3, TaF_5,BrF_3, BiF_5,BrF_3, AsF_5,BrF_3. From the solution of sulphur trioxide, SO_3,BrF_3 was obtained.[67] It has been seen above that bromine trifluoride has a conductivity remarkably higher than that of chlorine trifluoride or iodine pentafluoride. The solutions containing the foregoing complexes have an enhanced conductivity and bromine trifluoride is found to be an ionizing solvent.[70] The potassium fluoride complex is considered to ionize: $KBrF_4 \rightleftharpoons K^+ + BrF_4$, and is therefore described as potassium bromotetrafluoride, or tetrafluorobromite; its behaviour in respect of solutions in bromine trifluoride is that of a base. The sodium, silver and barium complexes are equally regarded as bromotetrafluorides and as bases. The other soluble fluorides ionize with the metal in a complex anion, and it is considered that the positive ion is 'fluorobromonium,' BrF_2^+. Thus, with the niobium complex, $NbBrF_8$, $BrF_2{\cdot}NbF_6 \rightleftharpoons BrF_2^+ + NbF_6^-$, and this 'acid' is systematically designated fluorobromonium hexafluoroniobate.[66] The evidence for this description is found in the ability to carry out electrometric titrations and neutralization reactions. Thus, typical of any acid base neutralization, when a bromine trifluoride solution of fluorobromonium hexafluoroantimonate is added continuously to a solution of potassium tetrafluorobromide, the conductivity decreases to a minimum, which is the point of equivalence, $KBrF_4 + BrF_2{\cdot}SbF_6 \rightarrow KSbF_6 + 2BrF_3$, and then increases.[70] The solubility of auric fluoride has already been mentioned, and this solution contains the acid fluorobromonium tetrafluoroaurate which, when added to a solution of silver tetrafluorobromite, gives a precipitate of silver tetrafluoroaurate: $AgBrF_4 + BrF_2{\cdot}AuF_4 \rightarrow AgAuF_4 + 2BrF_3$. Many complex fluorides have been made (see below) by the agency of bromine trifluoride, even from components having no great solubility in the solvent. The compounds obtained may not be always separable in a pure form as there is a tendency to retain the solvent which is attributed to solvolysis or to incomplete reaction.[85]

Potassium bromotetrafluoride is a white crystalline compound, obtained by evaporating off excess bromine trifluoride in vacuo at room temperature. Its stability is demonstrated by the fact that it only loses 0·5% in weight in these conditions over a period of six hours.[61] The *X*-ray diffraction pattern is different from that of potassium fluoride: the structure has been likened to that of the iodotetrachloride, $KICl_4$, but the order of stability in the bromotetrafluorides, $K>Na>Rb>Cs$, is the opposite of that in other known polyhalides, and this is attributed to the relatively small size of the BrF_4^- ion, which is equivalent to a cube of 4·84 A. side, compared with 6·66 A. for the ICl_4^- ion.[4] Potassium bromotetrafluoride loses bromine trifluoride rapidly above 280°C., whereas the sodium, rubidium and caesium compounds decompose appreciably as solvent is removed at ordinary temperatures. The compound can be kept in glass for some time, but there is a slow evolution of bromine, and it reacts with water rapidly, though not so violently as bromine trifluoride. In the reaction with water, free bromine and oxygen are formed, but some bromic acid remains in the solution. On heating the salt in a platinum crucible, a brown product, platinic fluoride, is formed, although platinum is unattacked by boiling bromine trifluoride. The other bromotetrafluorides which have been prepared show similar reactions.[61] Conductivities of solutions of the potassium, silver and barium salts have been determined for various concentrations and temperatures.[70] On applying direct current in the conductivity cell, no decomposition voltage could be observed, but the current–voltage relation did not follow Ohm's law: the same brown colouration at the cathode and the same sharp boundary between this and the yellow solution was observed, as with bromine trifluoride itself. Among the fluorobromonium acids, the gold compound, $BrF_2{\cdot}AuF_4$, is formed in solution by the action of bromine trifluoride on gold or on auric chloride.

On evaporating excess solvent in vacuo at 50°C. the compound is obtained as a yellow solid, which loses bromine trifluoride slowly at 120°, rapidly and quantitatively at 180°C. This is recommended as a method for making auric fluoride. The bromine trifluoride complex reacts with water, with carbon tetrachloride, benzene, and ethyl alcohol.[65] Difluorobromonium hexafluoroplatinate $(BrF_2)_2PtF_6$ is obtained as a red solution by the reaction of bromine trifluoride with platinic chloride or bromide. The 'acid' decomposes rapidly at 180° to 200°, giving platinic fluoride. The corresponding rhodium compound decomposed too rapidly at ordinary temperatures to be isolated.[71] The product obtained by the reaction of bromine trifluoride with tin compounds and evaporation of the solvent was unstable. On evacuating for a given time at 15°, 35°, 100°, and 190° the ratio of bromine trifluoride to stannic fluoride was, respectively, 1·76, 0·75, 0·46 and nil; but the solution was presumed to contain difluorobromonium hexafluorostannate, $(BrF_2)_2SnF_6$, from the data on conductivity, from the formation of hexafluorostannate, and from neutralization reactions. It was not possible to carry out a titration, but mixtures of potassium and tin salts in varying proportions were allowed to react when dissolved in bromine trifluoride and the conductivity was minimal at the ratio corresponding to K_2SnF_6.[70] Titanium tetrafluoride behaves similarly, being soluble in bromine trifluoride, but it was not possible to isolate the solute, $(BrF_2)_2TiF_6$. Potassium hexafluorotitanate was shown to dissolve readily in bromine trifluoride, and on evaporating the solvent the analysis of the product corresponded to K_2TiF_6,1·1 BrF_3. The *X*-ray powder-photograph showed this product to contain potassium bromotetrafluoride, so that this is an example of solvolysis.[85] By the action of bromine trifluoride on arsenious oxide, a solution was obtained from which only arsenic pentafluoride (volatile) could be recovered. But, for example, treatment of silver arsenate with bromine trifluoride gave a clear solution containing, presumably, silver hexafluoroarsenate and excess silver bromotetrafluoride.[72] From antimony compounds, on the other hand, it was possible to isolate fluorobromonium hexafluoroantimonate, $BrF_2{\cdot}SbF_6$, which on heating in vacuo for 2 hours at 40°C. lost only 0·1% in weight. It can be stored in dry Pyrex glass for several months without appreciable attack, but it fumes in moist air and reacts with water. A conductimetric titration was carried out with silver fluoride in a similar manner to that described above for potassium and tin, and the minimum corresponded with $AgSbF_6$. On electrolysis of the bromine trifluoride solution of fluorobromonium hexafluoroantimonate, the behaviour was the same as with potassium bromotetrafluoride.[70] Bismuth pentafluoride is sparingly soluble in bromine trifluoride, and on removing excess solvent a white hygroscopic solid was obtained; after five hours at 25°C. in vacuo the product lost 16% in weight, and after one hour in vacuo at 50°, 70°, 100° and 120° lost, respectively, 23·9%, 51·1%, 83·2% and 100% in weight. Hexafluorobismuthates prepared in this solvent showed solvolysis.[66] From the clear solutions obtained by the action of bromine trifluoride on niobium and tantalum or their pentoxides products were obtained analysing as fluorobromonium hexafluoroniobate and hexafluorotantalate, and these compounds showed considerable stability. Thus the niobium compound lost nothing in weight after 6 hours in vacuo at 30°C., 7·2% at 50°, and after one hour at 100° and 120°, and 1·5 hours at 150°C., lost, respectively, 14·5, 47·7 and 91·6%. The tantalum compound after 1 hour at 100°, 120°, 150°, 175° and 200° lost, respectively, 5·4, 8·1, 19·3, 43·7 and 71·7% by weight, being thus the more stable.[66]

It has been seen how complex fluorides are prepared by the neutralization reactions described above. Some of these show solubility in bromine trifluoride, though on evaporation they undergo solvolysis. But even when the acid, or the base, or the complex derivative, is insoluble, treatment of a mixture of materials, suitably chosen, with bromine trifluoride is a valuable means of preparing complex fluorides, some of which may not have been previously prepared. The following preparations from bromine trifluoride in this way may be mentioned: lithium hexafluoroniobate from lithium carbonate and niobium, with lithium chloride the reaction was incomplete; sodium hexafluoroniobate from sodium carbonate or fluoride, and the potassium salt from the carbonate, chloride or fluoride, and niobium; the rubidium and caesium salts from their bromides, and the silver salt from silver metal or silver chloride and niobium; calcium hexafluoroniobate from calcium fluoride and niobium, but barium chloride and niobium gave a partly solvolyzed product. Tantalum derivatives were prepared very similarly; with calcium fluoride the reaction was incomplete and the barium product was solvolyzed. Silver hexafluorobismuthate was obtained from silver and fluorobromonium hexafluorobismuthate; alkali metal products were solvolyzed, though the potassium hexafluorobismuthate less so than the sodium compound.[66] From sodium and potassium metaphosphate, the hexafluorophosphates were obtained; sodium orthophosphate gave sodium hexafluorophosphate and an excess of ill defined sodium bromotetrafluoride. The action of silver orthoarsenate has been mentioned above. Metal halides and phosphorus pentachloride gave mixtures of hexafluorophosphates and bromotetrafluorides, but phosphorus pentabromide gave quantitative yields of hexafluorophosphates.[72] This method of preparation has been the subject of a separate paper.[68] It is there shown that complex fluorides of boron, phosphorus, arsenic, and antimony can be prepared by mixing equivalent amounts of suitable substances, which will give the corresponding bromine trifluoride acid and base, and treating them with this reagent: the free elements, the oxides, carbonates and halides may be used, or, less generally, an oxyacid salt in which the elements occur in the desired proportions. It was not possible, however, to prepare complex fluoro-salts of aluminium, indium, thallium, zirconium, hafnium, thorium, lead, bismuth, selenium, tellurium, molybdenum, tungsten, uranium, iodine or manganese, owing to insolubility in bromine trifluoride or because of solvolysis.[68] Borax gave sodium fluoborate, the excess boron escaping as the trifluoride. Potassium persulphate and pyrosulphate gave the fluorosulphonate, KSO_3F (see below). Nitrates alone gave fluorides or bromotetrafluorides, and nitric oxides, but when they were mixed with an 'acid'-forming constituent nitronium salts were obtained; *e.g.*, potassium nitrate and boric oxide gave a mixture of potassium and nitronium bromotetrafluorides, $KBrF_4$ and NO_2BrF_4. It was shown also that by mixing dinitrogen tetroxide and an 'acid' forming substance and treating the mixture with bromine trifluoride, nitronium complex fluorides in general could be obtained. Bromine trifluoride reacts with potassium chloride and silica to give a mixture of potassium fluosilicate and bromotetrafluoride, and this of course suggests that all the salts prepared in silica vessels may be contaminated to a greater or less extent. Usually the loss in weight of the silica flask in any one experiment was not great, only a few milligrams, but it increased to the order of 100 mg. in making nitronium compounds owing, it was said, to the corrosive action of nitronium fluoride, NO_2F. The behaviour of the sulphur oxyacid salts, $M_2S_2O_x$, is related to their structure.[72] Where the structure is such as to permit the formation of fluorosulphonates, these are formed, but otherwise the bromotetrafluorides are formed. Thus potassium persulphate and pyrosulphate give the fluorosulphonate. But potassium pyrosulphite $K_2S_2O_5$ and thiosulphate $K_2S_2O_3$ give one molecule of fluorosulphonate and one of bromotetrafluoride: potassium sulphate and silver sulphate give the same, whilst sodium dithionite, $Na_2S_2O_4$, gave the bromotetrafluoride, as did sodium sulphite. In addition to the formation of nitronium salts referred to above which are derivatives of the nitronium ion, NO_2^+, there have also been prepared nitrosyl complexes derived from the ion NO^+, which the authors suggest should be renamed nitrosonium.[67] Whilst by analogy with the formation of nitronium salts from dinitrogen tetroxide the nitrosonium salts should be made from nitric oxide, they were actually made from nitrosyl chloride as being more convenient to handle. Nitrosyl chloride and bromine trifluoride gave, with boric oxide, nitrosonium fluoborate $NO{\cdot}BF_4$; with phosphorus pentabromide, the hexafluorophosphate $NO{\cdot}PF_6$; with germanium dioxide, the hexafluorogermanate $(NO)_2GeF_6$; with stannic fluoride, the hexafluorostannate $(NO)_2SnF_6$; with silica, a mixture of indeterminate composition; with gold, the tetrafluoroaurate $NO{\cdot}AuF_4$; with titanium tetrafluoride, the hexafluorotitanate $(NO)_2TiF_6$. In addition, from the chloro-compound $(NO)_2SnCl_6$ the corresponding fluoro-compound was obtained, but $NO{\cdot}BiCl_4$ gave bismuth trifluoride. Nitrosyl pyrosulphate (from dinitrogen tetroxide and sulphur dioxide in a sealed tube reaction), $(NO)_2S_2O_7$, was freely soluble in bromine trifluoride, and from the solution was obtained the fluorosulphonate, $NO{\cdot}SO_3F$, identical with the product from nitrosyl chloride and fluorosulphonic acid. A number of other reactions also are described in this paper.[67]

Finally, the action of bromine trifluoride on potassium dichromate, silver dichromate and potassium permanganate gave, respectively, the compounds $KCrOF_4$, $AgCrOF_4$, and $KMnF_6$. It is noteworthy that whilst it has been impossible to obtain manganese tetrafluoride alone, it is here stabilized in a complex. The removal of oxygen from vanadium pentoxide and vanadates by bromine trifluoride is usually slow, owing to the formation of undefined oxygen-containing complexes, and this is not a good route to hexafluorovanadates; but from nitrosyl chloride, vanadium pentoxide and bromine trifluoride, 'nitrosonium' hexafluorovanadate was prepared.[74]

BROMINE PENTAFLUORIDE

Bromine pentafluoride, although it is better characterized than the monofluoride, has perhaps received even less attention. There is only one paper dealing in detail with its properties, that of the discoverers, Ruff and Menzel,[54] but there are some half dozen others where some mention of its properties is made. When Ruff had established that there was a chlorine trifluoride as well as a monofluoride, he looked for higher fluorides of the other halogens and thus found first iodine heptafluoride and then bromine pentafluoride. Attempts to prepare the pentafluoride in platinum apparatus, by reaction of the trifluoride with fluorine, led to trouble with corrosion, even when pure platinum was used instead of platinum-iridium alloy. Gold also was unsatisfactory for the same reason. Copper, however, was found to be resistant, and the production directly from bromine and fluorine was convenient. A vertical copper tube, with a thermocouple pocket entering from the lower end, was maintained at 200°C.; fluorine was led into the upper end, and bromine carried in a stream of nitrogen was also led in at this end, the tube projecting into the reactor. The bromine feed rate was 6 cc. vapour per minute, the fluorine 35 cc. per minute. The gases leaving the apparatus were condensed in silica, and in 7 hrs. about 12 cc. of crude product was obtained. Emeléus has mentioned using a temperature of 250°C. for the preparation.[5] Booth and Pinkston say that the method of Ruff and Menzel is essentially that used at present;[2] other workers have mentioned obtaining supplies of the compound in steel cylinders.[3,86] Ruff and Menzel purified the crude product by fractional distillation at 150 mm. pressure in an all-silica apparatus without contact with tap grease or organic matter. The fractionating column was immersed in ice. The crude product gave a fore-runnings fraction of 19% consisting of silicon tetrafluoride, a red decomposition product of bromine trifluoride and water, and about 70% of pentafluoride; there followed 72% of the main fraction of pure pentafluoride, leaving 9% of residue containing bromine trifluoride with 25% of pentafluoride. The crude product had thus contained 87·5% of pentafluoride.

BROMINE PENTAFLUORIDE: PHYSICAL PROPERTIES

Bromine pentafluoride, when pure, is a colourless liquid, fuming strongly in air; the effect of attack by moisture is to cause colouration increasing through yellow to deep red. The gas density at 29°C. and 330 mm. pressure was 174·7, compared with a calculated value of 174·92. The analysis, made by breaking a small silica bulb containing a small sample of the liquid in 20% caustic soda solution contained in a platinum flask closed with a rubber stopper and then determining fluorine and bromine, corresponded with the formula BrF_5. The melting point was −61·3°C. The vapour pressure between −88° and +24° was measured in silica apparatus with a silica spiral manometer. For the solid the vapour pressures were 0·1 mm. at −88° and 1·7 mm. at −65°, for the liquid the vapour pressure was given by $\log_{10} p_{mm} = 8{\cdot}0716 - \dfrac{1627{\cdot}7}{T}$ and some typical values were:-

t °C	−59·3	−42·1	−30·5	−20·8	−10·8	0	+9·1	17·3	21·8	24·0
p_{mm}	3·0	10·6	22·8	41·7	73·0	130·3	203·1	293·2	356·5	390·3

The b.p., by extrapolation, was 40·5 ± 0·5°C.; the latent heat of evaporation, 7,443 g.-cal./g.mol.; Trouton's constant, 23·7; the critical temperature approximately 197°C. The density of the liquid at the m.p. was 2·763 g./cc. and in general, $d = 3{\cdot}496 - 0{\cdot}00346T$(°K.). The density of the solid at the m.p. was approximately 3·09.

A study of the nuclear magnetic shielding of bromine pentafluoride shows (see page 227) that the structure is a tetragonal pyramid, like that of iodine pentafluoride.[86] Experiments employing the radioactive isotope ^{18}F show that very rapid exchange of fluorine atoms occurs between bromine pentafluoride and hydrogen fluoride in the vapour phase at ordinary temperatures.[3] The electrical conductivity has recently been measured.[87] The compound is completely miscible with liquid hydrogen fluoride.[43]

BROMINE PENTAFLUORIDE: CHEMICAL PROPERTIES

Ruff and Menzel gave a long list of reactions of the pentafluoride with solid elements; the reactivity is very similar to that of the other halogen fluorides considered, and very violent reactions may occur in appropriate circumstances. As has been previously remarked, the precise character of the reaction must depend on the degree of fineness, the possibility of contamination, and other factors. It has been noted above that bromine trifluoride has been supplied in steel cylinders, so that massive iron is as resistant to this compound as it is to the other halogen fluorides, and in general the behaviour of metals, for handling purposes, will be the same as for other halogen fluorides. The behaviour of platinum, which Ruff found satisfactory for making bromine trifluoride at low temperatures but was corroded when making the pentafluoride at higher temperatures, corresponds with what has been reported under bromine trifluoride regarding platinum and also gold. Copper was more resistant under these conditions, but attention is again drawn to the risk of serious corrosion of this metal at temperatures above 300°C.

Many oxides, halides, and other salts reacted violently as did strong sulphuric acid and strong nitric acid, and fire and explosion were likely to occur with hydrogen or compounds containing hydrogen such as hydrogen sulphide, ammonia, methane, acetic acid, alcohol, benzene; and also cork, paper, waxes, greases, etc.

The reaction of bromine pentafluoride with water is very violent but can be carried out in a controlled manner, *e.g.*, by carrying water vapour in a stream of nitrogen into the liquid, which then assumes a deep red colour. It was at first considered that an oxyfluoride was formed by partial hydrolysis, *e.g.* $BrF_5 + H_2O \rightarrow BrOF_3 + 2HF$, but it was shown subsequently that all the oxygen of the water introduced was liberated as free oxygen. When the red liquid was distilled at 0°C., under reduced pressure, a deep red distillate came over just before bromine pentafluoride distilled; the remainder was pure pentafluoride which distilled completely as such. The deep red distillate separated into two layers, a lighter coloured upper layer which was pentafluoride with a little bromine, and a deep red lower layer which was bromine containing 6·5% of fluorine and so, evidently, contaminated with a bromine fluoride. The incomplete miscibility of bromine and its fluorides was thus demonstrated, but the existence of a lower fluoride in the bromine layer was suspected. When the red liquid was distilled very slowly at −50°, the growth of red crystals in the distillate was observed, together with liquid pentafluoride. The crystals melted one degree below the m.p. of pure bromine and gave a pale brown gas which when analysed gave a fluorine : bromine atomic ratio of 2. When a mixture of bromine and its pentafluoride was fractionally distilled, the bromine distilled over in the first fraction although its boiling point is 19° higher than that of pentafluoride. This led Ruff and Menzel again to conclude that a lower fluoride was being formed, and in a later paper they suggested that bromine monofluoride was present in labile equilibrium. The evidence was unconvincing, and is really consistent with the view that free bromine is liberated when bromine trifluoride and water react: $2BrF_3 + 5H_2O \rightarrow Br_2 + 10HF + 2\frac{1}{2}O_2$; alternatively, if bromine monofluoride is formed, the reaction is presumably $BrF_3 + 2H_2O \rightarrow BrF + 4HF + O_2$.

Mixtures of bromine pentafluoride with chlorine explode on heating; the mixture with bromine, which may possibly form monofluoride at ordinary temperatures, yields the trifluoride when heated in a copper tube at 250°C. With iodine, immediate reaction occurs, with evolution of heat, giving iodine pentafluoride. The only other chemical reaction of bromine pentafluoride reported, apart from these results of Ruff and Menzel, is that it converts cobaltous chloride to a mixture of cobaltous and cobaltic fluoride in the ratio 45 : 55, whereas bromine trifluoride gives the ratio 55 : 45; iodine pentafluoride gives 72% of the cobaltous salt and chlorine trifluoride gives wholly the cobaltic salt.[2]

IODINE PENTAFLUORIDE

This is the halogen fluoride with the longest history. Mellor (II,114) said that it was first prepared by Gore in 1875, though the true date was 1871, and this is generally accepted as the original discovery. It has been suggested that the compound was first prepared by Kammerer in 1862,[2] but it will be seen below that this was actually the first preparation not of the pentafluoride but of the heptafluoride. Iodine pentafluoride is also remarkable in that it is formed by reactions other than the direct combination of the elements. Gore's first preparation, from silver fluoride and iodine, was of this character, and other reactive or higher metal fluorides may be substituted for silver fluoride. Ruff suggested the use of cobalt trifluoride[9] and the formation of iodine pentafluoride by the action of iodine on ruthenium pentafluoride has been described.[88] Ruff and Menzel described the vigorous action of iodine on bromine pentafluoride,[54] and the formation of the pentafluoride from iodine oxy-compounds has been noted in several cases. The action of fluorine on iodine pentoxide gives the pentafluoride[89] but the reaction is rapid only above 250°C.:[90] iodine reacts more readily with bromine trifluoride, whilst iodates also react easily with this compound,[72] and in particular manganous iodate reacts vigorously with liquid bromine trifluoride.[74]

Ruff suggested that iodine pentafluoride could be made and handled in glass,[9] but a little later copper apparatus was described by Ruff and Keim; dry iodine was placed in a wide, watercooled copper tube and fluorine was passed over it.[91] Immediate reaction occurred and the liquid product, containing dissolved iodine, was collected in a narrower water-cooled copper tube, the passage of fluorine being continued until the product was decolorized. Copper apparatus has been used also by other workers,[92] and Ruff and Braida said that direct reaction gave such a rise in temperature that silica glass could not be used unless the fluorine were diluted with, say, three times its volume of nitrogen.[93] When iodine reacted with fluorine thus diluted, in transparent silica, the course of the reaction could be watched and the brown solution observed. In decolorizing this, occasionally a sudden very temporary blue colour was observed, but no explanation of this could be offered. If the temperature was allowed to rise too high, or if there was much oxygen in the fluorine, iodine oxytrifluoride, IOF_3, crystallised from the crude product on cooling. There was also likely to be some heptafluoride present, and this could be removed either by adding iodine until a slight colour appeared or by distilling in silica at 10 mm. pressure when the fraction collecting about 10°C. was the desired product. The production in silica in a platinum boat has been mentioned, with redistillation in a stream of fluorine,[56] but this might be expected to lead to contamination with heptafluoride. The preparation has also been described by Emeléus and co-workers. Quantities up to 30 g. were made by passing fluorine over iodine contained in a silica vessel partially immersed in water and continuously shaken to avoid formation of an inactive surface layer.[50] The product is decolorized by passing excess of fluorine over the liquid, and is redistilled immediately before use.[35] Production in a nickel vessel has been mentioned, with distillation at 20°C. and 5 mm. pressure,[94] conditions remarkably different from those used by Ruff. It has also been stated that iodine pentafluoride, handled in a fluorine-resistant glass ('Fluorex' - see page 137), when distilled sometimes had a pale yellow to pale blue colour, attributed to free iodine produced by reaction with the glass:[95] this may, however, have referred to the use of ordinary glass before the 'Fluorex' vessel became available, and a water-white product was obtained by bubbling in iodine heptafluoride. Mention has been made of the compound being supplied commercially, but no indication was given of the preparative method.[3,86] In a process recently described, fluorine was passed into iodine contained in a nickel vessel having a motor driven stirrer.[96]

IODINE PENTAFLUORIDE: PHYSICAL PROPERTIES

It has been seen above that, although there is a tendency to develop colour, the pure liquid is water-white.[95] It freezes to white crystals.[92] The melting point has been given (Mellor II,114) as −8°, whereas the correct figure is +8°C. Moissan's value. The value −8°C. has also been reported recently, and it is surmised that this was again a misprint, for otherwise the compound, apparently identified by its m.p., could not have been iodine pentafluoride.[90] The melting point has been variously given as 8 – 9°,[91] 10°,[92] and, in a paper by Ruff and Braida on which we are dependent for most of the known physical properties, 9·6°C.[93] The vapour pressure of the solid between −5° and the m.p. is given by $\log p_{mm} = 11{\cdot}764 - \frac{3035}{T}$, and of the liquid up to 70°C. by $\log p_{mm} = 8{\cdot}83 - \frac{2205}{T}$.[93] The same method was used as for bromine pentafluoride, viz., by means of a quartz spiral manometer in silica apparatus up to 20°C., keeping down the concentration of silicon tetrafluoride by frequent freezing and evacuation, and by the Smith-Menzies method up to 70°C., using sulphuric acid as the containing liquid in spite of its slight reaction with iodine pentafluoride. The results cannot be completely reliable, but the boiling point, by extrapolation, is given as 98° ± 1·5°C. The results are shown in Table IX. The liquid density is given by $D = 4{\cdot}38 - 0{\cdot}004T$ (°K.), individual values being as shown in Table X.[93]

TABLE IX. - VAPOUR PRESSURE OF IODINE PENTAFLUORIDE

	Solid				Liquid						
temperature, °C.	–5	0	5	9	15	20	30	40	50	60	70
pressure, mm.	2·8	4·7	7·0	10·2	15·0	20·0	36·2	57·2	99·2	159·4	253·1

TABLE X. - DENSITY OF IODINE PENTAFLUORIDE

	Solid	Liquid						
temperature, °C.	0	0	4	8	9·6	15	25	35
density, g./cc.	3·754	3·290	3·273	3·255	3·252	3·231	3·189	3·140

Some values given are for the supercooled liquid. The solid density at –193°, determined by liquid oxygen displacement, was 4·07. The electrical conductivity has been determined by Emeléus et al.[35] Using the same method as for bromine trifluoride, the results were less reproducible, those for two samples differing by about 10% and ranging from 1·61 and 1·78 × 10^{-5} ohm^{-1} cm.^{-1} at 10°C. to 2·30 and 2·55 × 10^{-5} at 25°C. With less rigorously purified material, results as high as 5 – 6 × 10^{-5} were obtained. As distinct from bromine trifluoride, the liquid has a positive temperature coefficient of electrical conductivity. When 0·1 g. of iodine was introduced into 40 cc. of the pentafluoride it gave a dark brown solution, even though incompletely dissolved, and increased the electrical conductivity, the resistance of the cell falling from 2296 to 2000 ohms. It was not possible, on applying direct current, to observe a decomposition voltage, although the conductivity did not follow Ohm's law and at higher voltages free iodine was liberated at the cathode. Woolf obtained an appreciably lower conductivity, 1·53 × 10^{-5} ohm^{-1} cm.^{-1} at 25°C., presumably indicating better purification.[97] As is indicated below, the conductivity is enhanced by certain solutes.

The structure of iodine pentafluoride has been considered.[4] From electron diffraction studies it was found that all the I – F distances were equal and, assuming a trigonal bipyramid, the bond length was 2·56 A.[92] As the sum of the covalent radii of iodine and fluorine is 1·97 A., this result seems open to question. From infra-red absorption and Raman spectra, evidence has been obtained for an arrangement as a tetragonal pyramid, with four fluorine atoms at the corners of a square base and the iodine atom and the odd fluorine atom on a fourfold axis normal to the base.[95] The electronic configuration in this structure has been considered[98] and support for it has also been found from a study of the nuclear magnetic shielding.[86] Radioactive tracer studies with ^{18}F show that rapid exchange of fluorine atoms occurs in the liquid phase between iodine pentafluoride and hydrogen fluoride,[3] and, as might be expected, these compounds are completely miscible.[43,97]

IODINE PENTAFLUORIDE: CHEMICAL PROPERTIES

Iodine pentafluoride is the only halogen fluoride for which the reaction with water has been quantitatively studied: in this instance the heat of hydrolysis has been determined by breaking a Pyrex glass ampoule containing the pentafluoride under a large excess of water in a calorimeter. Prideaux showed in 1906 that iodic acid was formed quantitatively, and Woolf has now shown that the reaction $IF_5 + 3H_2O \rightarrow HIO_3 + 5HF$ is exothermic to the extent of 22·05 kg.-cal. at 18°C.[94] From this the heat of formation of iodine pentafluoride was calculated to be 205·3 kg.-cal. The heat of hydrolysis in 0·25 N-caustic potash was also determined; 118·9 kg.-cal. are evolved in this reaction, and this gives the heat of formation as 204·2 kg.-cal.

The general chemical properties were described by Ruff and Keim.[91] Like the other halogen fluorides, iodine pentafluoride reacts violently with water, water-containing materials and many organic materials, and with elements and metals in an appropriate condition for reaction, usually finely divided. Its fuming in moist air is due to hydrolysis. It attacks soft glass, slowly at ordinary temperatures, rapidly at the boiling point, silicon tetrafluoride and iodine pentoxide being formed. Dry silica glass is more resistant, but not completely so. No evidence could be found of an oxyfluoride being formed during hydrolysis. Later workers have referred to the rapidity of the reaction with glass above 30°C.[90] A slow reaction occurs between thionyl chloride and iodine pentafluoride, leading to the formation of a thionyl chlorofluoride, and with carbon monoxide at 120 atm. pressure the pentafluoride slowly forms carbonyl chlorofluoride.[28] Iodine pentafluoride is partially soluble in 1:4-dioxan, and from the solution the compound $IF_5,C_4H_8O_2$ has been isolated, melting with decomposition at, or above, 112°C.[99] The reaction with iodoform, to yield fluoroform and iododifluoromethane, $CHIF_2$, has been reported, and it was also said that with carbon tetraiodide hexafluoroethane was formed.[100] This last statement is probably a case of mistaken identity, as Emeléus et al. have shown that trifluoroiodomethane is obtained.[63] It was shown that carbon tetrabromide also reacted gradually with iodine pentafluoride on heating at 90°C. for three hours, the products being largely tribromofluoro- and dibromodifluoromethane, with a little tetrafluoromethane. Ruff and Keim found that when iodine pentafluoride is formed in situ from iodine and fluorine in the presence of carbon tetrachloride, mixed fluorochloromethanes are formed.[91] In the reaction of iodine pentafluoride with tetraiodoethylene, too rapid admixture gave explosions but by adding the pentafluoride carefully pentafluoroiodoethane was obtained. The reaction was carried out in glass, and the reaction products included carbon dioxide, silicon tetrafluoride, and tetrafluoroethylene.[63] The reaction of di-iodotetrafluoroethane with iodine pentafluoride to yield pentafluoroiodoethane has also been described.[101]

As a solvent, iodine pentafluoride shows properties similar to those of bromine trifluoride, but in a limited range, and the solvolysis that occurs in formation of salts, even with bromine trifluoride, is more pronounced with iodine pentafluoride. The iodine pentafluoride system has not, however, been explored as fully as that of bromine trifluoride and any general conclusions must be guarded. Potassium fluoride dissolves in iodine pentafluoride; a 1% solution was obtained at the b.p., and on cooling, a white crystalline salt was deposited.[50] On removing the excess solvent at 2 – 5 mm. and 15 – 20°C., the product analysed as KIF_6, potassium iodohexafluoride: it melts at about 200°C., but is then rapidly losing iodine pentafluoride, and even at room temperature is decomposes at pressures below 1 mm. The compound reacts readily with water, less readily with dioxan: it also reacts with acetone, and with carbon tetrachloride on warming. Since IF_6^-, like SeF_6 and TeF_6, is presumably octahedral, and the expected electronic configuration of its iodine atom is $5s^2 5p^6 5d^4 6s^2$, it is predicted that the interhalogen distance will be found to be abnormally large.[50] Antimony pentafluoride was readily soluble in hot iodine pentafluoride and on removing excess solvent in the usual way a hygroscopic white solid, analysing as $SbIF_{10}$, was obtained.[97] This compound, m.p. 103° with slight decomposition to yield a blue liquid, is formulated as $IF_4^+.SbF_6^-$ The compound obtained by interaction of solutions of potassium fluoride and antimony pentafluoride and subsequent careful evaporation still retained some solvent, and analysed, *e.g.*, as $KSbF_6,0{\cdot}23IF_5$: this result was attributed to solvolysis. The electrical conductivity of iodine pentafluoride is much enhanced by these solutes. Thus with 0·045 g.-moles of antimony pentafluoride per 1000 g. solvent, the conductivity was 114×10^{-5} ohm.$^{-1}$ cm.$^{-1}$ at 25°C. and 93×10^{-5} at 12·5°C., compared with $1{\cdot}53 \times 10^{-5}$ for the pure solvent. Stannic fluoride was insoluble. Boron trifluoride was soluble, the saturated solution having a conductivity of $3{\cdot}55 \times 10^{-5}$ ohm.$^{-1}$ cm.$^{-1}$ at 25°C., and by passing the gas into a solution of potassium fluoride in iodine pentafluoride potassium fluoborate was obtained. Sulphur trioxide was freely soluble and the solution showed enhanced conductivity: on distilling various mixtures the fraction of maximum boiling point (145 – 7°C./759 mm.) was found to have the composition $IF_5,1{\cdot}17SO_3$, and hence was a constant boiling mixture rather than a compound. It was not possible to obtain potassium fluorosulphonate by adding potassium fluoride to the sulphur trioxide solution. Potassium persulphate was insoluble, but retained some solvent (*e.g.*, $K_2S_2O_8$, $1{\cdot}02IF_5$). Potassium metaphosphate was partially soluble, but no fluorophosphates were obtained – one product analysed as $KPO_3,2{\cdot}3IF_5$. Potassium iodate was readily soluble, but no oxygen was evolved and on evaporation the solvent was strongly retained, to the extent of half a mole or more per mole of potassium iodate. Data have been given for the variation of conductivity with concentration for potassium iodate solutions, which in this respect behave like a salt in aqueous solution.[97] The solubility of iodine oxytrifluoride in iodine pentafluoride has already been noted above.[93] Iodine pentafluoride does not appear to form stable complexes with hydrogen fluoride, so that on evaporating excess hydrogen fluoride in a stream of nitrogen the residue from a solution is only the pentafluoride, and no potassium iodohexafluoride was obtained by the interaction of iodine pentafluoride and potassium hydrogen fluoride in hydrogen fluoride solution.[97]

IODINE HEPTAFLUORIDE

In describing the formation of iodine pentafluoride by the action of fluorine on iodine, Moissan said that by varying the conditions and by using either an excess of fluorine or an excess of iodine he had never obtained a gaseous iodine fluoride. But thirty years later Ruff and Keim, in distilling iodine pentafluoride made from fluorine and iodine or its pentoxide, always found a more volatile fraction and were led to identify the heptafluoride, which is a gas at room temperature.[89] Booth and Pinkston[2] have suggested that Kammerer, in studying the reaction of iodine and silver fluoride, was probably the first investigator to prepare iodine pentafluoride,[102] Kammerer, using very carefully dried material and equipment, warmed iodine with excess of argentous fluoride in an evacuated sealed glass tube, at 70 – 80°C. The iodine colour disappeared, the glass remained unetched and, on breaking the tube under mercury, a gas was collected which was completely absorbed by caustic potash. He could find no trace of silica or iodine in the potash solution, and concluded that he had prepared fluorine, which was thus shown not to attack glass. He had difficulty in explaining why no oxygen had been liberated – possibly, he thought, hydrogen peroxide or potassium hyperoxide had been formed, as he concluded that the formation of a fluoric acid was inconceivable. The description is enough to show that he must have prepared iodine heptafluoride, and is as much a tribute to the excellence of his experimental technique as to the inadequacy of his conclusions. He would not, of course, find iodine by a simple test if it were present in solution as the periodate. This observation, however, was lost sight of for almost 90 years and Ruff and Keim were the first to separate and characterize the compound. Ruff also suggested that he had indications of the existence of an iodine fluoride lower than the pentafluoride, but nothing more has been reported about this.[18]

There has been little work on the heptafluoride, apart from the original paper of Ruff and Keim, and a more recent paper on the preparation and some properties.[96] The earlier paper stated that fluorine was passed over the pentafluoride maintained at 90°C., and the mixture passed through a platinum tube at 270 – 300°C., the pentafluoride being condensed at ordinary temperatures

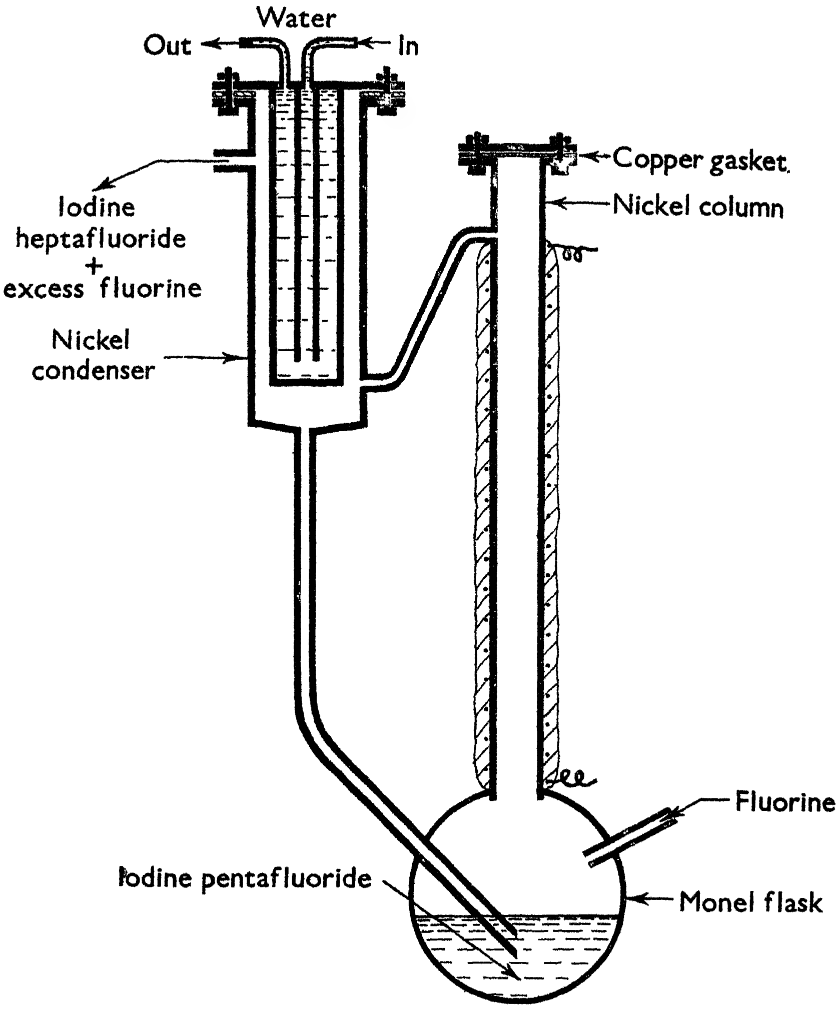
Water
Out
In
Copper gasket.
Nickel column
Iodine heptafluoride + excess fluorine
Nickel condenser
Fluorine
Iodine pentafluoride
Monel flask

Fig. 3. APPARATUS FOR THE PREPARATION OF IODINE HEPTAFLUORIDE

and the heptafluoride in refrigerated traps. In a later arrangement, using an all platinum apparatus, fluorine was passed over iodine in a water cooled reactor which was occasionally shaken: the reactor had a vertical platinum outlet tube which could be heated to 250 – 270°C., and a side tube from this was water cooled so that excess pentafluoride was refluxed and returned to the reactor.[89] In the later paper, a similar apparatus of nickel was used.[96] A nickel flask had a side inlet for fluorine, and a long vertical neck, electrically heated, closed with a removable soft copper gasket (Fig.3). Below this a side arm connected to a water cooled nickel trap, from the base of which ran a return pipe to the flask. This apparatus could be used to make pentafluoride, for which purpose a stirrer was inserted down the neck into the flask, which was ice-cooled. To make heptafluoride, pentafluoride was put in the flask, warmed to 70 – 80°C., the column was heated to 280 – 290°, and fluorine was supplied at the rate of 8 – 12 g. per hour. The heptafluoride was condensed out in Monel metal traps cooled with solid carbon dioxide, and, using an excess of fluorine, was obtained in almost 100% yield on iodine. The crude iodine heptafluoride was subjected to high vacuum at –90°C., and was then sublimed, in absence of air, to separate it from any pentafluoride.[89] Schumb and Lynch also purified the heptafluoride by a similar trap-to-trap distillation, using Monel metal traps, distilling from one warmed to 0°C. into another cooled to –78°.[96] The compound is a colourless solid, which sublimes, with a vapour pressure of 760 mm., at 4·5°C. The vapour pressure is given by the equation $\log_{10} p_{mm.} = 8{\cdot}6604 - \frac{1602{\cdot}6}{T}$, the latent heat is estimated to be 7·33 kg.-cal./g.mole and Trouton's constant is 26·4; these rather high figures are taken to indicate some polymerization of the solid. Under slight pressure the solid melts at 5 – 6°C. to a colourless liquid the density of which is 2·8 g./cc. at 6° and 2·7 g./cc. at 10°. The molecular weight corresponding to the vapour density was 266·2 (calculated for IF_7 = 260·3).[89] From the infra-red and Raman spectra of the compound it has been concluded that the molecule has the form of a pentagonal bypyramid, a structure not met with in any other compound. The iodine atom is at the centre of a regular pentagon of fluorine atoms, and two other fluorine atoms are equally spaced above and below this plane, on the axis of symmetry through the iodine.[95] The electronic configuration in this structure has been considered.[98] Chemically, iodine heptafluoride shows reactions similar to those of the other halogen fluorides, and Ruff and Keim give a long list of elements with which reaction occurred, but these should be carefully considered in the light of what has been said previously as to the extent to which the occurrence and character of reaction must depend on the conditions of the experiment, including the state of division, purity and dryness of the materials, the quantities taken, etc. To some extent, however, the reactions of iodine heptafluoride may be less violent. Thus on bubbling the gas into water, solution occurred quietly and was incomplete: periodic and hydrofluoric acids were formed in the aqueous solution. Many organic compounds react vigorously; carbon monoxide burns in the gas. Ammonium compounds react violently, sulphuric acid becomes effervescent and with iodine the pentafluoride is formed.[89]

A number of reactions have been examined in more detail.[96] In studying reactions in presence of copper at temperatures up to 300°C., it was noted that the attack on copper was much more pronounced than with fluorine alone, in agreement with what has been previously noted about the effect of chlorine and bromine in such cases. It was not found possible to obtain, from sodium and potassium fluoride and rubidium chloride, compounds of the form MIF_8; the rubidium chloride was partially converted into fluoride, but the other compounds were recovered unchanged. Reaction with dichlorodifluoromethane in presence of copper gauze, leading to replacement of one chlorine atom with fluorine, occurred to a small extent at about 350°C., but to a much greater extent in the presence of mercuric fluoride. No reaction occurred with chlorotrifluoromethane.

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SECTION VI.

COMPOUNDS CONTAINING FLUORINE, OTHER HALOGENS, AND OXYGEN.

By H. R. LEECH

Several chlorine oxyfluorides have been discovered in recent years: their nomenclature is somewhat unsystematic. The first to be discovered, made by treating perchloric acid with fluorine, was called fluorine perchlorate, $FClO_4$, by analogy with fluorine nitrate, FNO_3, although the authors agreed that this was not a very good name. The compound ClO_2F was not named by its discoverers. The discoverers of ClO_3F proposed the name chloryl oxyfluoride, $ClO_2.OF$, by analogy with nitryl oxyfluoride, $NO_2.OF$; and ClO_4F, it was suggested, should be called perchloryl oxyfluoride. There is a possibility of isomerism in this series, according to whether the fluorine atom is directly attached to the chlorine atom, $ClO_n.F$, or through an oxygen atom, $ClO_{n-1}.OF$. The latter must almost certainly be the case in ClO_4F, as in NO_3F and, from the stability of such compounds as F_2O and $CF_3.OF$, both the existence and the stability of the OF group are shown. It may be suggested that compounds containing this group should be named fluoroxides, by analogy with hydroxides, and thus if the acid radicles of chlorous, chloric, and perchloric acid are named chlorosyl, chloryl, and perchloryl respectively, we have the following series:

Radicle	Acid		Acid fluoride	Acid fluoroxide
	Hypochlorous,	$Cl.OH$	ClF	$ClOF$
Chlorosyl, ClO-	Chlorous,	$ClO.OH$	$ClO.F$	$ClO.OF$
Chloryl, ClO_2-	Chloric,	$ClO_2.OH$	$ClO_2.F$	$ClO_2.OF$
Perchloryl, ClO_3-	Perchloric,	$ClO_3.OH$	$ClO_3.F$	$ClO_3.OF$

It will be observed that each acid fluoride after the first is isomeric with the fluoroxide of the preceding member. The hydrolysis of the fluoroxides will give rise to acid peroxides (or per-acids), and this will presumably contribute to instability in the presence of moisture. No corresponding bromine compounds have been reported, and the only iodine compound in this class is the oxytrifluoride, IOF_3.

Chlorosyl Fluoride, $ClO.F$; *Chlorine Fluoroxide,* $Cl.OF$.

These compounds have never been prepared although their existence was suspected by Ruff, *e.g.*, as a product of the hydrolysis of chlorine trifluoride. In one case, from the product of reaction with water (in silica) there was obtained, in addition to silicon tetrafluoride, a red liquid solidifying at -70° thought to be $ClOF$.[1] In another case, in the reaction of chlorine with fluorine oxide, a reddish-brown solid was separated in the liquid air trap. On warming up, the compound exploded at about -10°. This might conceivably be the fluoroxide.[2] The compound $ClO.F$ would be isosteric with sulphur difluoride, SF_2, which has not been characterized, but of which the b.p. is probably between -40° and -100° C.

Chloryl Fluoride, $ClO_2.F$; *Chlorosyl Fluoroxide,* $ClO.OF$.

The controlled reaction of fluorine and chlorine dioxide was shown by Schmitz and Schumacher to lead to the formation of a compound ClO_2F, but this method of preparation affords no clue to its constitution.[3] Addition of fluorine causes chlorine dioxide to decompose explosively, but by diluting the gases with a considerable excess of nitrogen, combination occurs smoothly. Nitrogen was passed over pure redistilled chlorine dioxide at -50°C., when its vapour pressure is 25 mm., and fluorine was admitted from a reservoir held in liquid oxygen (pressure 2 atm.) to give a partial pressure of 50 mm. The gases were mixed in a 1 l. silica flask, and a contact time of 2–3 minutes was allowed. The exit gases passed through a liquid oxygen trap, where a crystalline solid collected. The product was very sensitive to moisture, *e.g.*, if admitted to silica apparatus which was not completely dry, reddish brown vapours were produced. The compound also seemed to react with glass and was, therefore, always handled in silica. The vapour pressure of a sample redistilled in vacuo was measured, and the following results, which were not regarded as very accurate, were obtained.

t °C.	–78	–65·5	–55	–45·5	–38·0	–30·2	–23·8	–17·2	–9·7	–6·3
p_{mm}	8·8	25·2	55·9	103·8	161·4	244	338	459	645	740

The m.p. is about -115°; b.p., about -6°; mean latent heat of evaporation, 6·2 kg.-cal./g.mol.; Trouton's constant, 23·2. On exposing the compound to moist air, dense white fumes are formed; and the authors considered it to be probably the fluoride of chloric acid, i.e., chloryl fluoride. Emeléus and Woolf suggested that this compound might be formed by the action of bromine trifluoride on potassium chlorate,[4] but this was before the discovery of ClO_3F was announced, and it seems more likely that the latter would be the product of their reaction. Chloryl fluoride would be isosteric with thionyl fluoride, b.p. -43·8°, and with phosphorus trifluoride, b.p. -101°.

Perchloryl Fluoride, $ClO_3.F$; *Chloryl Fluoroxide,* $ClO_2.OF$.

Fluorine reacts with sodium chlorate only above 200°C., to give the fluoride and chlorine, but with potassium chlorate it reacts between 140° and 180°C. to give white fumes, and rubidium and cæsium chlorates behave similarly [5] the presence of chlorine would not account for the white fumes. By carrying out the reaction at a lower temperature, 40°-60°C., Bode and Klesper were able to show that the so-called chlorine hexoxide, Cl_2O_6, was formed, thus offering a new method of preparing this compound. At lower temperatures still, ClO_3F was obtained. The potassium chlorate was contained in a U-tube of Jena glass, and the reaction was allowed to start at room temperature or could be facilitated by adding a little iodine. As soon as the white fumes appeared at the exit, the tube was plunged into a bath at -40°, and in this way there was obtained, in the liquid air trap, a white solid compound which melted at about -110° and boiled at about -40°C. Reaction with caustic soda gave equivalent quantities of chlorate ion and fluoride ion together with some oxygen, and it was suggested that the reaction was $ClO_3F + 2OH' \rightarrow ClO_3' + F' + H_2O + \frac{1}{2}O_2$. With fluorine at 80°–100°C. chlorine hexoxide was formed, $2FClO_3 \rightarrow F_2 + Cl_2O_6$, together with a little chlorine monoxide. The vapour pressure was measured, and the following values were obtained:

t °C.	–76	–70	–67	–65	–57	–50	–48
p_{mm}	224	237	269	305	460	639	706

These are represented by the equation $\log p = 4{\cdot}41 - 1000/T$. The b.p. is -46°; the molecular latent heat of evaporation, 4·6 kg.-cal.; Trouton's constant, 20·2. The m.p. was −110°, but no great purity was claimed for the product, and this may be too low. It is not obvious which of the isomers this compound is. The hydrolysis to chlorate suggests that it is the fluoroxide. The perchloryl fluoride would be isosteric with the compound SO_2F_2 (b.p. −55·4°), POF_3 (b.p. −39·4°) and SiF_4 (b.p. −95°), and the similarity of all these boiling points suggests that the compound prepared by Bode and Klesper is $ClO_3.F$ rather than $ClO_2.OF$. These authors stated that on carrying out the reaction of fluorine and potassium chlorate at −78°, a different compound was obtained; this was a glass at liquid air temperature, softened at −150° to an oily liquid, and boiled between −20° and −10°. On hydrolysis it went almost completely to perchlorate and fluoride, with gas evolution. It was pointed out that this reaction and the boiling point suggest 'fluorine perchlorate', but this compound had been described as crystalline in the solid state. On the other hand perchloryl fluoride would hydrolyze to perchlorate and fluoride. If the reaction consists, in the first place, in the production of a perchloryl radicle, $KClO_3 + \frac{1}{2}F_2 \rightarrow KF + ClO_3$, fluorine may add on either to the chlorine or to one of the oxygen atoms, giving either the perchloryl fluoride or the chloryl fluoroxide, and the proportions of these two compounds would depend on the temperature. Unfortunately, it would be expected that the more compact molecule, $ClO_3.F$, would have a lower boiling point than $ClO_2.OF$, whereas the chemical evidence suggests that the lower boiling compound is $ClO_2.OF$. Obviously more information is required.

Perchloryl Fluoroxide, $ClO_3.OF$ (Fluorine Perchlorate)

By analogy with the preparation of fluorine nitrate from fluorine and nitric acid, Rohrback and Cady studied the action of fluorine on perchloric acid.[6] In the first case, fluorine was passed up a water-jacketed glass column packed with glass chips down which 60% perchloric acid was dripped. From the liquid air traps on the exit line it was possible to separate from the oxygen, fluorine oxide, and silicon tetrafluoride, a white crystalline solid which finally gave a liquid, b.p. −15·9°/755 mm. The preparation was very inefficient; 100 cc. of acid gave only 1 cc. of liquid. By warming to 60°C., a slight improvement in yield was obtained. In an all-carbon apparatus none of this product was obtained, but by passing fluorine over the surface of 72% perchloric acid in a platinum boat, keeping the temperature at about 21°C., a 90% yield was obtained. The compound readily exploded, e.g., a small spark or flame at the mouth of an open-ended test tube containing the gas shattered the tube, and a little grease or dirt, or even rubber tubing, caused explosive decomposition. In one experiment, contact with potassium iodide solution caused explosion. For analysis, the vapour was allowed to diffuse through a column of air into potassium iodide solution, when the reaction $ClO_4F + 2I \rightarrow I_2 + ClO_4^- + F^-$ occurred: iodine, perchlorate and fluoride were determined to establish the composition. The vapour density at 25°C. gave a molecular weight of 120 (calculated for ClO_4F, 118·5). The compound had a sharp acid odour. On attempting to determine the freezing point, the compound tended to explode as it solidified, but in one experiment a f.p. of −167·3° was determined. Perchloryl fluoroxide is not isosteric with any known compounds. Attempts to prepare the corresponding iodine compound, IO_4F, from periodic acid led to the dehydration of the acid and then to the production of iodine pentafluoride.[7]

Iodine Oxytrifluoride, IOF_3

Mellor (II, 292) states that if iodic acid is dissolved in a solution of hydrofluoric acid in glacial acetic acid, colourless crystals of $IOF_3,5H_2O$ are obtained on evaporation. Ruff and Braida isolated the anhydrous compound, IOF_3, in the residues from the distillation of iodine pentafluoride, and said that it was formed from the oxygen present in the fluorine used to make this

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compound.[8] They also said that if the temperature during the preparation was too high and the attack on the silica apparatus correspondingly great, or if the fluorine contained a good deal of oxygen, then the iodine oxytrifluoride crystallized out on cooling. After distilling off the iodine pentafluoride at 10 mm. pressure and about -10°C., a crystalline residue remained, still retaining some pentafluoride which was removed by keeping it in a liquid-air cooled receiver in a high vacuum for 48 hours. Determination of iodine and fluorine in the compound, assuming the undetermined proportion to be oxygen, gave the formula IOF_3. Careful addition of water to iodine pentafluoride also gave the oxyfluoride, but the reaction is very violent and some pentoxide is also formed; there must be two reactions: $IF_5 + H_2O \rightarrow IOF_3 + 2HF$ and $2IOF_3 + 3H_2O \rightarrow I_2O_5 + 6HF$, and probably the equilibrium $5IOF_3 \rightleftharpoons I_2O_5 + 3IF_5$. On distilling off the pentafluoride, a mixture of the oxide and oxytrifluoride remains. Addition of pentoxide to the pentafluoride gives rise to the equilibrium above, a cold saturated solution yielding about 42% of the oxytrifluoride.

Iodine oxytrifluoride is obtained in fine white crystals which are hygroscopic, very soluble in water, and decomposed by moist air with evolution of hydrofluoric acid. On heating, the compound darkens at 200° owing to the separation of iodine, and above this temperature decomposition into iodine, oxygen, and iodine pentafluoride occurs; this is complete at 400°C. With hydrogen there is a slow formation of iodine, hydrofluoric acid and water. Reaction readily occurs with organic compounds (*e.g.*, benzene, alcohol), and with many metals.

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SECTION VII

COMPOUNDS OF FLUORINE WITH OXYGEN

By H. R. LEECH

When Mellor wrote his original work, he had to say that 'no oxygen compound of fluorine has yet been prepared'. Some question was raised by Moissan as to whether an unstable compound was not formed in the reaction of fluorine and water, and other workers had referred to this possibility. But a difluorine monoxide, F_2O, was reported by Lebeau and Damiens in 1927 as occurring in the fluorine obtained from their medium-temperature cell if the electrolyte was wet, and they later showed that the compound was readily made by bubbling fluorine through 2% caustic soda solution, a method which is generally employed. A difluorine dioxide, F_2O_2, was reported by Ruff and Menzel in 1933 to be formed when an electric discharge is passed through the mixed gases at liquid air temperature: the compound is completely dissociated below 0°C. According to a report by Aoyama and Sakuraba[40] in 1938, difluorine trioxide, F_2O_3, is formed by the action of ultra-violet light on a mixture of liquid oxygen and liquid fluorine, but still less is known about this compound. Ruff[1] and Ruff and Menzel[2] referred to the possible existence of another fluoride in the less volatile fractions remaining in the distillation of the difluorine monoxide, an observation which was confirmed by Cady,[3] but Ruff and Menzel seem to have satisfied themselves later that no new substance was present.[4] A more recent study of the reaction of fluorine with water vapour does, however, indicate the formation of unidentified oxidizing compounds.[5] It has also been suggested that salts of a fluorine oxyacid were formed by the action of fluorine on cold concentrated caustic alkali solutions[6] but it is more likely that chlorine oxyacids were formed from chlorine present as an impurity in the alkali.[7] There is no other report of any fluorine oxyacids, and fluorine monoxide shows no acidic properties.

FLUORINE MONOXIDE

Lebeau and Damiens were able to show that the fluorine from a medium-temperature cell, using their original electrolyte of composition KF,3HF, and a nickel or iron anode, was contaminated not only with oxygen, but also with a compound of fluorine and oxygen. Though they could not at first obtain the compound in a pure state, they showed that it was a gas, slightly soluble in water, having no action on glass, and probably of the formula F_2O.[8] In attempting to purify the gas, they examined the effect of washing it with caustic soda, and were thus led to the discovery that the compound was in fact formed by reaction of fluorine with 2% caustic soda solution.[9] Whilst the formation of fluorine oxide has been observed in a number of reactions, this is the preparative method which has always been used, with practically no change. Fluorine oxide is formed in reactions where the elements of water, if not water itself, may be regarded as present: an exception to this is the decomposition of an alkaline solution of nitroxyl fluoride, NO_3F (fluorine nitrate), made by the action of fluorine on nitric acid.[10] This compound dissolves in 2% caustic soda and slowly reacts, evolving fluorine oxide according to the equation $2NO_3F + 2NaOH \rightarrow 2NaNO_3 + F_2O + H_2O$.[11] When fluorine reacts with periodic acid dihydrate, the water is first removed and the evolved gases contain up to 27% of fluorine oxide.[12] This compound is also said to be formed by the action of fluorine on perchloric acid.[13] The products of the reaction of fluorine with water have been the subject of some dispute, and obviously the reaction is very sensitive to the conditions. Work in this field has already been considered under 'Fluorine' (see page 55). Ruff treated water vapour, diluted with carbon dioxide, with fluorine in a copper vessel at a temperature above 100°C.[1] No ozone was observed in the product condensed in liquid air, but he believed that, on fractional distillation, the fraction distilling between -170° and -160° was probably fluorine oxide, and that a small fraction melting between -35° and 0° was another fluorine oxide. Cady passed fluorine over ice, or over ice-cold water, and found that the major volatile product was oxygen but that some fluorine oxide was formed; if ozone is formed, he concluded, its importance as a product of the reaction had been overemphasized, for he could find none.[3] Later investigators agreed with Ruff that only fluorine oxide, hydrogen peroxide, hydrogen fluoride and oxygen were formed, and ozone, if at all, only in traces.[14] Briner and Tolun pointed out that Moissan and earlier workers may have identified as ozone what was in fact fluorine oxide,[15] but as ozone, if formed, could possibly undergo decomposition owing to the intense local heat of the fluorine reaction, they considered the possibility of lowering the temperature of the reaction with liquid water by employing solutions having much lower freezing points. They could find no ozone in the reaction gases from fluorine and water at 0°C., or in the product of reaction of fluorine with aqueous hydrofluoric acid, sulphuric acid or potassium nitrate at low temperatures, but 31% caustic potash at -55°C. did give about 1% of ozone. It was not clear whether this was a specific effect of the potash, which is known to form an ozonate. Ruff and Menzel identified some ozone in the residual liquid from the fractional distillation of crude fluorine oxide made by the fluorine-caustic soda process.[4] In all these reactions some fluorine oxide was formed, and fluorine oxide was always obtained from fluorine and water, whether or no the fluorine had been previously liquefied. This was contrary to an observation by Ruff, who stated that his yield of fluorine oxide (by reaction with caustic soda) fell to zero when the fluorine had been liquefied.[2] In the latest work on this subject, however, ozone has been identified in the products of reaction.[5] Fluorine and water vapour were allowed to react, in nitrogen as diluent, at room temperature and pressure using excess of fluorine: the reaction appeared to occur in two stages, one fast and one slow, and the formation of products stable in presence of fluorine and water was far from complete after 10 seconds. The products identified were hydrogen fluoride, oxygen, ozone, and hydrogen peroxide. There were probably some fluorine oxides, and the material evaporating from the condensation traps, at temperatures above -80° C., contained an unknown gas which had some of the characteristics of fluorine, was soluble in water and was suspected to be an oxygen-fluorine compound.

Cady found that the reaction of fluorine with solid hydroxides – those of sodium, potassium, calcium, and barium (octahydrate) – was variable.[3] At 0°C., the sodium and barium hydroxides reacted rapidly, much heat was liberated, the gaseous product was nearly all oxygen with an odour of fluorine oxide and the less volatile unidentified compound referred to by Ruff[1] was also present. At -78° the reaction would hardly start except on vigorous shaking, and as much as 30% of fluorine oxide was present in the gaseous products. Cady also studied the effect of concentration of caustic alkali on the formation of fluorine monoxide and found that with both caustic potash and caustic soda the yield is greatly dependent on the strength of the solution,

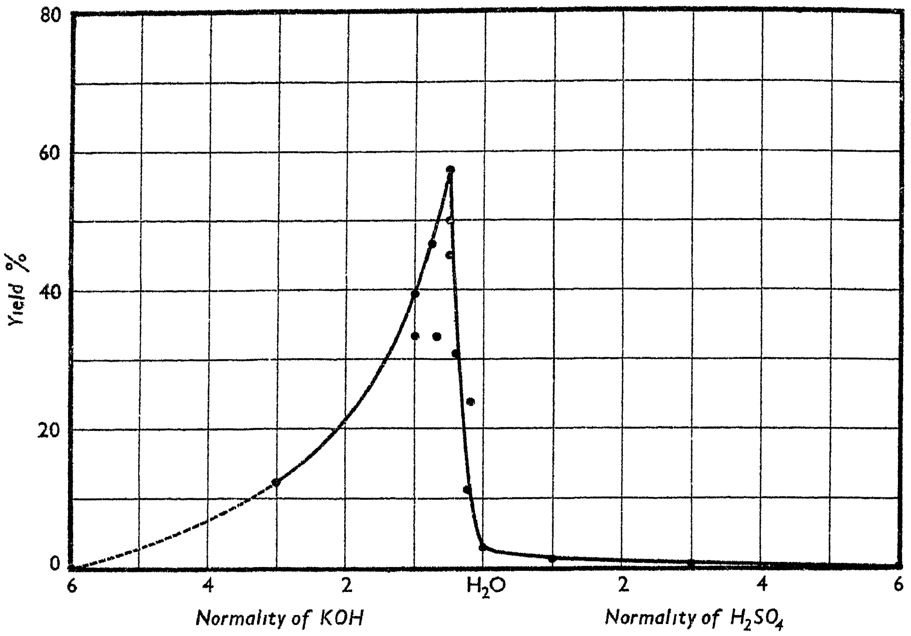

Fig. 1. YIELDS OF FLUORINE OXIDE PRODUCED BY THE ACTION OF FLUORINE ON AQUEOUS SOLUTIONS

as shown in Fig. I. The yield rises to a maximum of almost 60% in 0·5N-caustic potash which, he says, 'is about the same hydroxide concentration as the 2% sodium hydroxide used by Lebeau and Damiens'. The yield falls very steeply in the direction of lower alkalinity, being about 1% in a neutral solution, and somewhat less steeply in the direction of higher alkalinity, being still 40% for a 1·0N-solution and 10% for a 3N-solution. These reactions were carried out at 2°C. and it was found that, on shaking a solution of the desired strength with fluorine gas, the reaction took about 90 seconds for completion. It is obvious, however, that in this method of carrying out the reaction the alkalinity of the solution is changing throughout, and Cady does not say specifically what his alkalinities represent – whether they are the strength of solution at the beginning of absorption, the average alkalinity, or that finally reached. If the other product of reaction is mainly oxygen, the two principal reactions are $2F_2 + 2NaOH \rightarrow 2NaF + F_2O + H_2O$, and $2F_2 + 4NaOH \rightarrow 4NaF + 2H_2O + O_2$. In this reaction the volume of oxygen is half that of the fluorine, and therefore, for a yield of x% of oxide on the fluorine used, the percentage of oxide in the total gaseous product will be $200x/(100+x)$ and for Cady's 60% yield, the gaseous product will contain 75% of oxide and 25% of oxygen by volume. Most workers have reported less than this: Ruff and Menzel refer to a 45% yield;[2] others say the gas contained 50% of oxide, *i.e.* 33% yield;[16,17] or 60%,≡43% yield;[18] using 4% NaOH, the gas contained only 15% oxide, ≡ an 8% yield;[19] and recently 3% caustic soda has been used but no yield given.[20] Since the yield is very dependent on the

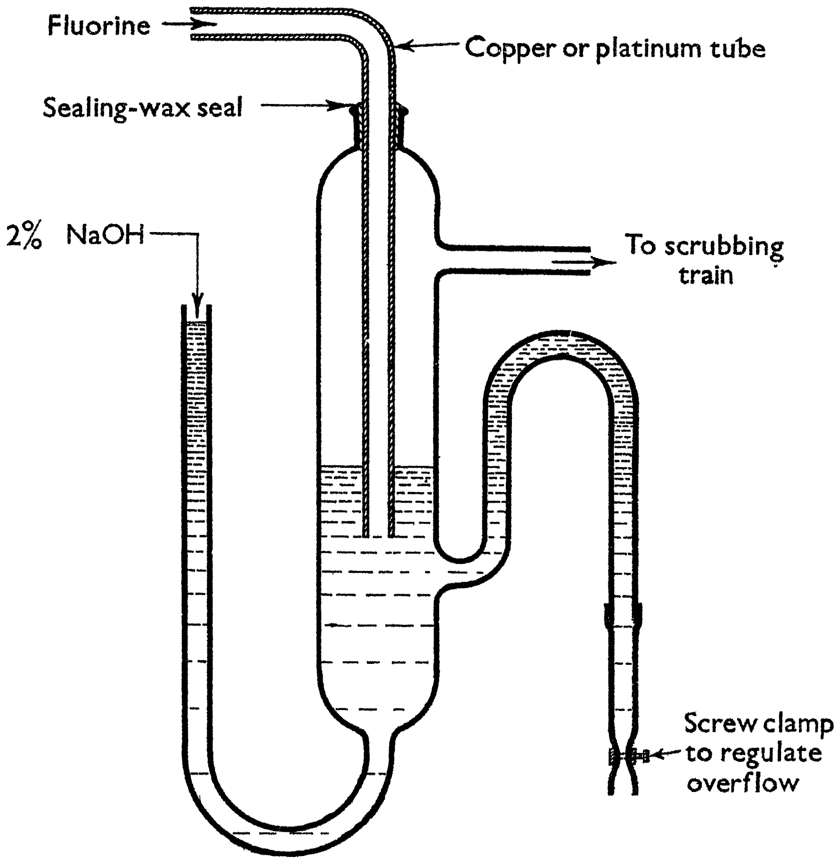

Fig. 2. REACTOR FOR FLUORINE OXIDE PRODUCTION

concentration of caustic soda employed, it must also depend on the ratio of caustic soda to fluorine in the reacting system. For this reason production is always carried out in continuous flow apparatus and in a study of the production using a large volume of 2% solution circulated through the reaction chamber (though little information is given) it is pointed out that the contact time between the fluorine and the caustic soda must be very short as on prolonged contact the fluorine oxide is decomposed.[21] The production of fluorine oxide has been described on a number of occasions[2,3,17,19,20] but there is very little variation in the method since its first description by Ruff and Menzel. A text-book description may be taken as typical.[17] The essential feature is a glass reactor (Fig.2) made of 1 inch diameter glass tubing, 6 inches long, provided with a bottom inlet for caustic liquor and an overflow at a little below half way up the tube. There is an upper gas outlet, and an inlet pipe of copper or platinum enters through the top and dips ¼ – ½ in. into the caustic liquor. Caustic liquor is fed through the reactor at the rate of 1 l./hr.; fluorine at the rate of 1 – 3 l./hr. The gas produced is washed with water and then passed through a trap cooled with solid carbon dioxide

Refs. p. 195

and into a liquid-air-cooled trap, where a pale yellow liquid collects. For purification, the crude condensate must be fractionally distilled in a low temperature column. Ruff and Menzel obtained finally a 40% yield of gas containing 98·5% of fluorine oxide[2] and later 99·8%.[4] By condensing in liquid oxygen and pumping down with a water-jet pump, a product containing 75% of oxide was obtained[19] whilst another similar preparation gave a product with 85% mol.-% of oxide.[17] By freezing in liquid nitrogen and pumping off oxygen, a purity of 96% was achieved.[20] Finally, by fractional distillation through a 3 ft. column, a middle fraction of substantially pure oxide was obtained – 99·6%, 100·02% by iodimetry.[20]

The physical properties of fluorine monoxide have recently been reviewed.[22] Ruff and Menzel said that at liquid-air temperature, a layer of the liquid 1·5 cm. deep was an intense yellow with a tinge of brown[2] but later the liquid has been described as pale yellow only.[17] The gas is colourless. There has only been one value reported for the melting point of the solid, -223·8°C. for a material only 98·5% pure.[23] The density of the liquid was given by Ruff and Menzel as 1·65 at -190°C.;[2] $d = 2{\cdot}1315 - 0{\cdot}004695\ T$ (°K.)[4]

In later work, the density at the boiling point has been given as 1·521, compared with 1·531g./c.c. from the above equation, and the density can be represented by $d = 2{\cdot}190 - 0{\cdot}00523\ T$: the mean density (liquid and vapour) is $1{\cdot}069 - 0{\cdot}00240\ T$, from which the critical density is 0·553 g./c.c.[24] The viscosity of the liquid is 0·2826 centipoises at –145·3°C., and $\log \eta = \frac{131{\cdot}5}{T} - 1{\cdot}5768$ where T is in °K., between –146° and –153°C.[24] The vapour pressure is given by the equation $\log p_{\mathrm{mm}} = 7{\cdot}3892 - \frac{578{\cdot}64}{T}$ and,[4] later, $\log p_{\mathrm{mm}} = 7{\cdot}2242 - \frac{555{\cdot}42}{T}$.[20] The first equation gives a b.p. of –144·8°C., the second –145·3°C., both obtained on samples 99·8 – 100% pure. From the first equation, the latent heat is calculated to be 2·650 kg.-cal./g.mol.; and Trouton's constant, 20·65. The critical temperature was found to be –58·0° ± 0·1°, the calculated critical pressure is 48·9 atm. and the critical density, 0·553 g./c.c[24] The thermodynamic properties, calculated from spectral data, are given in Table I.[25]

TABLE I - THERMODYNAMIC FUNCTIONS OF F_2O. - g.-cal./deg.mole.

T°K.	$-(F^\circ - H_0^\circ)/T$	S_0	C_p°
298·16	50·31	58·93	10·08
300	50·36	59·00	10·10
350	51·72	60·60	10·63
400	52·91	62·04	11·08
500	55·00	64·60	11·79
600	56·79	66·79	12·29
700	58·36	68·71	12·65
800	59·76	70·42	12·90
900	61·03	71·95	13·09
1000	62·20	73·34	13·23
1100	63·27	74·61	13·34
1200	64·26	75·77	13·42
1300	65·19	76·85	13·49
1400	66·06	77·85	13·54
1500	66·88	78·79	13·58

From electron diffraction studies, the F–O–F angle is estimated to be 100 ± 3°,[26] or 105 ± 5°,[27] and from a study of the infra-red spectrum, it is 100·6°.[28] The O – F distance is given as 1·4 ± 0·1A.[27] Spatial relations in fluorine oxide have been considered theoretically.[29,30] Ruff and Menzel expected, by anology with chlorine monoxide, that fluorine monoxide would be highly endothermic, but found that the compound could not be explosively decomposed by sparking, even using a heavy spark. They determined the heat evolved on burning the oxide in hydrogen and absorbing the products in dilute caustic soda, and calculated the heat of formation of the oxide as -4·6 ± 2 kg.-cal., so that the compound was slightly endothermic.[2] Von Wartenberg and Klinkott measured a number of heats of reaction and obtained discordant results for the heat of formation.[19] From the reaction with 40% caustic potash, $2KOH + F_2O \rightarrow 2KF + H_2O + \frac{1}{2}O_2$, the heat of formation was estimated to be -11·5 ± 2 kg.-cal.; from the reaction with potassium iodide solution acidified with hydrofluoric acid, $4HI + F_2O \rightarrow 2HF + H_2O + 2I_2$, a value of -8·0 ± 2 kg.-cal. was obtained, and the reaction with 45% hydrobromic acid gave the value -14.8 ± 1.7 kg.-cal.: the figure -11.9 ± 2 kg.-cal., was considered the most probable. Ruff and Menzel suggested a revised figure of -9.2 kg.-cal.;[31] von Wartenberg favoured the value -9 kg.-cal.[32]

Fluorine monoxide is a relatively stable compound, in the sense that it cannot be detonated by sparking, but the influence of water vapour is important. Von Wartenberg found that when confined over sulphuric acid a gas of 25% fluorine monoxide content (the remainder being oxygen) could not be detonated between platinum points, but when the gas was kept over water, violent explosion occurred with mixtures containing 25–70% F_2O, and a gas containing only 12% F_2O exploded weakly.[19] In these explosions 80 – 90% of the oxide present at the higher concentrations decomposed, but only 50% of that present in the milder explosions of weaker mixtures. It was suggested that in the presence of moisture hydrofluoric acid was formed, and that the much greater heat evolved in this reaction led to explosion. A study of the spectrum suggested that one absorption maximum was to be attributed to dissociation of the molecule into two particles, either (F_2 + O) or (F + FO), and another to complete breakdown into the constituent atoms,[33] and this led to a study of the photochemical dissociation. The oxide, contained in a water cooled silica vessel, was irradiated with a quartz mercury vapour lamp, and the change of pressure was observed. Decomposition occurred, but no appreciable quantity of free fluorine was found, all the fluorine appearing as silicon tetrafluoride: dissociation presumably produces fluorine atoms which, unlike fluorine molecules, attack the silica vessel. The thermal decomposition was then studied; vessels of glass, silica, magnesium, copper and silver were used, and the reaction was shown to be homogeneous.[16] Again, silicon tetrachloride was formed when this was possible, but when hard glass was used some fluorine was retained in the walls as silicofluoride. The copper and silver vessels showed steady fluorine absorption over many days, but the magnesium vessel was extraordinarily good, and in this case the fluorine produced by decomposition of the oxide remained uncombined. The reaction was unimolecular but followed a second order rate:-

$$-\frac{d[F_2O]}{dt} = k_1[F_2O]^2 + k_2[F_2O][O_2] + k_3[F_2O][SiF_4] + \ldots k_x[F_2O][X]$$

where X is an added gas – helium, argon, or neon – for which collison yields were obtained.

Fluorine oxide has been shown to be soluble in water, and the solution obeys Henry's law, with an absorption coefficient of 0.04297 at 20°.[34] Ruff and Menzel gave a value of 0·068 at 0°.[4] Reaction occurs in the liquid phase, however, and the solutions are not stable although the rate of reaction is slow, so that this, rather than the rate of solution, controls the overall rate of disappearance of the gas.[4,34] In the case of dilute caustic soda, on the other hand, reaction is rapid, and the rate of solution is the controlling factor.[34] The rates of reaction with various concentrations of caustic soda solution have been studied, and expressed as a rate equation for a first order reaction with $K = 0{\cdot}34$ min.$^{-1}$ for 10% NaOH at 29°, 0·10 min. for 1% NaOH at 59° and 0·045 min.$^{-1}$ for 1% NaOH at 21°C. Agitation causes a considerable increase in reaction rate.[18] It has been shown that, in the reaction with caustic soda, all the oxygen is liberated as gas and no oxidizing compounds remain in solution: the reaction is, therefore,[19]

$$F_2O + 2NaOH \rightarrow 2NaF + H_2O + O_2$$

and the gas does not behave as an acid anhydride. The reaction with caustic soda was used by Ruff and Menzel as an analytical method; the gas was shaken with 10% NaOH for 20 minutes, and fluorine was then determined in the solution.[2]

Fluorine oxide, like fluorine, the halogen fluorides and oxygen, is a powerful oxidizing agent; it reacts readily with oxidizable aqueous solutions and with organic compounds; it does not react readily at ordinary temperatures with solids which can form a protective coating, and is generally considered less reactive than fluorine.[4] A whole series of reactions was reported by Ruff and Menzel.[4] The stability of glass towards fluorine oxide was noted, and this material has been generally utilized in its production and handling but it has been noted that at temperatures of the order of 250°C. glass is attacked and silicon tetrafluoride, or fluosilicates, formed. A quartz filament, when heated to redness previously, will burn brightly in a stream of fluorine oxide.[4] Metals in finely divided form usually reacted on gentle warming, when of course, owing to dissociation, fluorine atoms may be present. Silver blackens, gold turns brown, mercury acquires a film (and on boiling gives a yellow fluoride) and even metals of the platinum group all glow and form fluorides when gently warmed in the gas. Mixtures of the halogens and fluorine oxide exploded on gentle warming and when the mixture with chlorine was passed through a copper tube at 300°C., reaction proceeded in a series of puffs or more violent explosions, chlorine monofluoride being formed although the reaction was incomplete. In one experiment a solid reddish-brown substance collected in the liquid air trap after the reactor, and exploded on warming up to −10°. This, it was suspected, might be chlorine monoxide or the chlorine oxyfluoride which Ruff often observed but never isolated. In another case, it has been reported that solid iodine is converted to iodine oxides.[21] Many compounds also reacted vigorously when gently warmed;[4] antimony pentachloride and titanium tetrachloride did not form any known oxyfluorides or oxychlorides but gave complex fluorochloro-derivatives. Sodium chloride and carbonate gave the fluoride, as did sodium nitrite and potassium nitrate. Calcium oxide reacted only on heating strongly. Phosphorus pentoxide, arsenious oxide, aluminium chloride, and chromic oxide reacted vigorously. Plumbous oxide gave lead peroxide and fluoride, mercuric chloride, the oxyfluoride. Many reducing gases exploded on sparking, but in some cases slow reactions occurred. Sulphur dioxide slowly gave the trioxide; hydrogen sulphide exploded on mixing; ammonia formed white fumes and slowly deposited ammonium fluoride; nitric oxide slowly turned brown, etching the glass, suggesting the formation of nitrosyl and nitryl fluorides.

Ruff and Menzel[4] also showed the powerful oxidizing action of fluorine oxide on aqueous solutions: from silver nitrate a higher oxide, Ag_2O_2, was precipitated; manganous sulphate yielded hydrated manganese dioxide. In alkaline solution, Cr^{III} ions were oxidized to chromate; from hydrogen sulphide, sulphur was precipitated; potassium ferrocyanide was oxidized in a complex manner. The reaction with acidified potassium iodide,

$$F_2O + 4HI \rightarrow 2I_2 + 2HF + H_2O,$$

was first used by Ruff and Menzel as an analytical method; the reaction goes rapidly to completion, and the determination of iodine gives a ready means of estimating fluorine oxide.[2] Von Wartenberg and Klinkott also examined a number of the reactions of fluorine oxide, and showed that whilst hydriodic acid reacted very rapidly, the reaction was less rapid with hydrobromic acid, and was slow with hydrochloric acid.[19] Reducing substances such as zinc, sodium sulphite, stannous chloride, ferrous sulphate, sodium thiosulphate and arsenious oxide reacted slowly, but were activated so that oxygen in the fluorine oxide was also absorbed. Ammonia in aqueous solution did not go completely to nitrogen; some was converted into nitric acid. The oxidation of aqueous solutions of stannous chloride, sodium arsenite, ferrous sulphate and potassium sulphite has also been reported.[35] Amongst organic compounds, benzene and paraffinic compounds absorb the gas completely; in the former case hydroquinone and quinone were formed, no phenol or pyrocatechol being observed.[19] Though little reaction with methanol, ethanol, benzene or carbon tetrachloride could be observed at room temperature, the gas dissolved in carbon tetrachloride and half of it had reacted in 48 hours. The distribution coefficient between water and carbon tetrachloride was examined, and anomalous results were obtained.[21] No uses have developed for this oxide of fluorine, and no reactions have been found of particular interest in preparative chemistry. It has, however, been suggested that difluorine monoxide has peculiar advantages as an oxidizing agent in rocket propellants.[36]

DIFLUORINE DIOXIDE

The possible existence of other fluorine oxides and fluorine oxy-acids has been referred to above, under 'Fluorine Monoxide'. Ruff had referred to the residue obtained on distilling his crude difluorine monoxide and, in his search for a higher compound, he examined this further.[4] The residue was separated by distillation into three fractions, which were examined separately. The first, boiling between -145° and -128°, proved to be a mixture of the monoxide and carbon tetrafluoride arising from the graphite anode in his fluorine cell. The second, boiling between -128° and -55°, but mostly distilling about -110°, was blue, and could also be identified by its smell as being principally ozone. The third, distilling between -55° and -51°. proved difficult to analyse, but it could only be concluded that it was largely made up of hexafluoroethane and sulphuryl fluoride. In a further search to find a higher compound – the idea being to make OF_4 – a mixture of fluorine and fluorine oxide was heated to 300° over potassium fluoride, and was also passed through an ozonizer; the monoxide was also heated with chlorine trifluoride; in no case, however, was any evidence obtained of a new compound.[4] Two years later it was shown that another oxide was formed on sparking together oxygen and fluorine at low temperatures.[37] A mixture of fluorine and oxygen at low pressure (about 15–20 mm. pressure of each gas) was passed through a silica vessel where a glow discharge was maintained whilst cooling with liquid air. An orange-coloured solid deposit appeared on the walls of the vessel, and melted to a cherry-red liquid at about -160°. It was possible to distil it under reduced pressure, so long as the temperature was not allowed to exceed -100°C., and the vapour was pale brown. On warming above -100°C., however, decomposition afforded a colourless gas.

The first product was characterized as difluorine dioxide, F_2O_2, and the thermal decomposition product was said to be FO.[37] A little later Ruff, in showing the formation of this orange-red deposit as a lecture demonstration, said that he had used the reaction as a means of removing oxygen from fluorine, which is certainly a very elegant application.[38] Larger quantities of the oxide were made in the brush discharge, either from a large inductor with a Wehnelt interruptor, or with 50-cycle alternating current, appropriately stabilised, from a transformer. There were differences in the performance with these two discharge methods, and also with the proportions of fluorine and oxygen used, these factors affecting the yield so that the removal of oxygen from fluorine was only achieved by the first method.[39] It has also been stated that difluorine dioxide is formed when a liquid mixture of the monoxide and oxygen is irradiated with ultra-violet light, or when liquid oxygen and fluorine gas are subjected to the silent electric discharge.[40]

The melting point of difluorine dioxide is $-163{\cdot}5°$C.; the density is given by $d = 2{\cdot}074 - 0{\cdot}00291\ T$ (°K.), determined between $-87°$ and $-156°$. The vapour pressure, below $-100°$, corresponds with the equation $\log p_{mm} = 7{\cdot}515 - \frac{1000}{T}$, from which the boiling point, by extrapolation, is $-57°$C.[39] Above $-100°$C., however, the vapour pressure does not fall on this curve, owing to decomposition into the colourless gas which was described as OF. This gas was said to differ from a mixture of oxygen and fluorine by its complete reaction with acidified potassium iodide; values for the m.p., vapour pressure, and density were given, and some chemical properties, said to be very similar to those of fluorine, were described.[39] However, two years later Ruff announced that this 'oxide' was a mixture of fluorine and oxygen.[41] Shortly afterwards Frisch and Schumacher, who had studied the kinetics of the dissociation of the dioxide, published a similar statement and claimed that Ruff was already aware of their intention to do so.[42] These authors gave a separate account of their attempt to identify the compound FO.[43] They confirmed the ready preparation of the dioxide, but found that the colourless decomposition product had the absoprtion spectrum of $F_2 + O_2$, rather than that of a new compound 2FO. They showed also that a synthetic mixture of fluorine and oxygen was absorbed by 30% hydriodic acid in exactly the same way as the decomposition product from the dioxide. The acid and the gas had to be carefully mixed or flames appeared, but if care were taken there was a rapid initial reaction corresponding to absorption of the fluorine followed by a slow reaction, taking over an hour, when oxygen was absorbed. Ruff and Menzel had relied on this absorption as proof of the existence of FO, and this new evidence made it certain that difluorine dioxide dissociates into fluorine and oxygen.

In their kinetic studies Frisch and Schumacher[44,45] made the dioxide using fluorine, from which the hydrogen fluoride had been removed, and carefully purified oxygen. The whole apparatus was of silica, the discharge vessel being 20 cm. long. As energy source, they used first a large inductor supplied with 500 cycle alternating current, and later a transformer on the 50 cycle supply, giving 0·07 amp. at 5000 volts in the secondary circuit. The upper electrode was water cooled and the 2 mm. copper wire of the lower electrode was cooled by the liquid air in which the lower part of the reactor was immersed. The gases were drawn through the apparatus by a water pump, the diaphragm valve on the fluorine supply being set to deliver a quantity equivalent to 6 amp. on the fluorine cell. (A sulphuric acid-filled bubble counter on the fluorine supply had to be taken out, as the spray from it reduced the stability of the fluorine dioxide). The oxygen supply was adjusted so that the discharge was thin and red, and a good yield was so obtained. If too much oxygen was supplied, the discharge ceased; the best proportion of fluorine to oxygen was 1:1. The decomposition was studied by measurement of the pressure change, since there is a doubling of the pressure on decomposition; $F_2O_2 \rightarrow F_2 + O_2$. It was found that glass was strongly attacked even at low temperatures, and the whole apparatus was therefore made of silica. The reaction was studied between -25° and -60°C., with starting pressures of between 20 mm. and 400 mm.; it was shown to be unimolecular and homogeneous; the activation energy was 17·3 kg.-cal. The influence of foreign molecules was also studied and it was shown that only with oxygen was the activation probability enhanced.[45] Fluorine dioxide can exist only transiently as room temperature is approached, and there have been no other reports of its formation. The hypothetical molecule FO has been the subject of theoretical treatment.[46]

DIFLUORINE TRIOXIDE

It has been reported that when a liquid mixture of fluorine monoxide and oxygen is illuminated with ultra-violet light, a solid consisting of the dioxide and a new compound, F_2O_3 is obtained.[40] It is also claimed that the same compound is formed when liquid fluorine and liquid oxygen are submitted to ultra-violet radiation.[47]

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SECTION VIII

FLUOROCARBONS AND RELATED COMPOUNDS.

By G. M. DYSON

NOMENCLATURE AND SCOPE

The term 'fluorocarbon' connotes compounds of carbon and fluorine only; if part of the fluorine in such a structure is replaced by another halogen the substance is called a 'fluorohalocarbon' (*e.g.* $C_5F_{10}Cl_2$). There has been some confusion concerning the use of 'perfluoro'; Haszeldine and Sharpe[1] state that it signifies 'that all the hydrogen atoms in the compound have been replaced by fluorine'. This is not in conformity with the usage which confines the use of 'perfluoro' to those compounds in which all hydrogen atoms directly attached to carbon only are replaced by fluorine. The latter is the more convenient usage and will be followed throughout this section, so that, for example $CF_3{\cdot}CF_2{\cdot}CF_2{\cdot}OH$ will be perfluoropropanol, and $CF_3(CF_2)_6COOH$, perfluorooctanoic acid. The large number of perfluoro compounds already prepared and the apparently limitless scope for future preparations makes the development of a convenient nomenclature necessary. Strictly speaking, compounds of carbon containing fluorine belong to the domain of organic chemistry and may be named by rules commonly used in that subject; this occasions no difficulty in simple instances where only one or two fluorine atoms are present, as in 1-fluoropropane, or 1,5-difluoropentane. The complete fluorination of such structures does not make normal systematic nomenclature impossible, it merely makes it cumbrous, as in 1,1,1,2,2,3,3,3-octafluoropropane or, *a fortiori*, 1,1,1,2,2,3,3,4,4,5,5,5-dodecafluoropentane; this difficulty can be overcome by the 'perfluoro' convention set out above. The real difficulty arises when a structure contains many fluorine atoms, but is not fully 'perfluorinated', as in $CF_3{\cdot}CFCl{\cdot}CF_2{\cdot}CF_3$ (2-chloro,1,1,1,2,3,3,4,4,4-nonafluorobutane) or in $CF_3{\cdot}CFH{\cdot}CFH{\cdot}CF_2{\cdot}CF_3$ (1,1,1,2,2,3,4,5,5,5-decafluoropentane); these names are cumbrous, but the substances cannot be named by the 'perfluoro' convention.

Simons[2] proposed to overcome this difficulty by using, for all perfluoro compounds, new names made by inserting the syllable 'for' in an appropriate place in the systematic or accepted name of the corresponding carbon-hydrogen compound; thus, CF_4 methforane, C_2F_6 ethforane, $C_{10}F_{22}$ decforane, $CF_2{=}CF_2$ ethforene, $CF{\equiv}CF$ ethforyne, CF_3COOH, acetforic acid. Any deviations from complete perfluorination could then be indicated as substituents into the 'for' name; thus, the two examples given above would be 2-chlorobutforane and 2,3-dihydropentforane. This principle, of denoting a perfluoro compound by a special 'mark' applied to the name of the corresponding C–H structure, has much to recommend it; whether or not the 'mark' proposed by Simons is the most convenient and generally acceptable has yet to be determined. Some authors place Φ before the name of the corresponding unfluorinated structure to indicate perfluorination, as in Φ-indan, C_9F_{16}.

The scope of this section covers the fluorocarbons and perfluoro-compounds, together with the fluorohalocarbons and such highly fluorinated structures, still retaining some hydrogen, as may be necessary to complete the study of the fully fluorinated compounds. Since Dumas and Péligot[3] prepared the first organic fluorine compound - methyl fluoride - in 1835 little was done in the field until Moissan's isolation of fluorine, in 1886, made the use of direct fluorination a possibility. Even then, despite the important pioneer work of Swarts, highly fluorinated compounds were comparative rarities until the advent of the modern fluorine cell, and the large-scale production of anhydrous hydrofluoric acid and the higher metallic fluorides enabled fluorination to be controlled. Now it seems clear that the majority of organic structures have their analogous perfluoro compounds and that these are not just hypothetical possibilities but are comparatively easily prepared. We have, therefore, to contemplate another chemistry - similar to organic chemistry and quite as extensive - in which hydrogen (except in a few functional groups) has been replaced by fluorine; and if we take account also of the innumerable highly, though only partially, fluorinated structures that may exist it is apparent that in time the scope of fluorine chemistry could equal or even exceed that of classical organic chemistry.

PREPARATION

The principal methods of preparing highly fluorinated organic structures are:

1. Direct fluorination of carbon.
2. Direct fluorination of organic compounds in the liquid or vapour phase.
3. Fluorination with higher inorganic fluorides, e.g. AgF_2, CoF_3, CeF_4 or MnF_3.
4. The interchange of the fluorine of anhydrous hydrofluoric acid with the chlorine of organic chloro-compounds, under the catalytic influence of inorganic fluorides such as SbF_5, AgF_2 and FeF_3.
5. The electrolysis of solutions of organic compounds in anhydrous hydrofluoric acid (the electrochemical method).

1. DIRECT FLUORINATION OF CARBON

Ruff and Keim[4] subjected purified wood charcoal to a stream of fluorine in which it burned to give mainly carbon tetrafluoride, CF_4, with some C_2F_6 and C_3F_8 and a small proportion of high-boiling residue which had the molecular formula C_6F_{12}. The direct fluorination of graphite gave similar results, with more of the higher-boiling products. Ruff and Bretschneider[5] showed that decolorizing carbon or graphite, at a temperature just below ignition point, absorbed fluorine to form a substance with the apparent composition[6] of a polymeric carbon monofluoride $(CF)_n$. This compound decomposes violently at higher temperatures to give free carbon and a mixture of fluorocarbons. *X*-Ray data support the view that this substance is a true chemical individual.[113] On the other hand, Simons and Block,[7] using approximately 1% of mercurous or mercuric chloride to moderate the violence of the interaction of fluorine and finely divided carbon, obtained a series of perfluoro paraffins.

2. DIRECT FLUORINATION OF ORGANIC COMPOUNDS

The violent explosions encountered when attempts were made to fluorinate hydrocarbons in the liquid phase with elementary fluorine, led to the earlier experiments being conducted with halocarbons, which are more tractable. Thus, Ruff and Keim[8] studied the fluorination of carbon tetrachloride, demonstrating that the violent and sometimes explosive course of this reaction could be moderated by passing the fluorine just above the surface of the boiling liquid, to which a trace of iodine had been added and in the vapour of which the fluorine burned quietly. An even better method was to pass the vapour of the tetrachloride mixed with fluorine and nitrogen over a higher inorganic fluoride as catalyst (*e.g.* CoF_3). A mixture of $CFCl_3$, CF_2Cl_2, CF_3Cl and CF_4 is obtained; if the proportions of CCl_4 and F_2 are equimolecular, these products are present in the proportions 6:9:3:1. One complication, common to this reaction and to others in which he substance to be fluorinated contains chlorine, is that chlorine monofluoride itself is formed and may also act as a fluorinating agent.

With hydrocarbons containing more than one carbon atom the energy liberated during direct fluorination is more than adequate to fracture the C–C bond, so that direct fluorination of a C_n hydrocarbon leads to a mixture of all the perfluoro compounds from CF_4 to C_nF_{2n+2}.

Bockmüller[9,10] studied the direct fluorination of a wide variety of organic substances, isolating in the main only partly fluorinated compounds; this method was also examined by Bigelow[11,12] who obtained many new perfluoro compounds. During the course of this work it became clear that vapour-phase fluorination offered considerable practical advantages over fluorination in the liquid phase. The discovery by Fredenhagen and Cadenbach[13] that vapour-phase fluorination can be conducted safely if the fluorine delivery tube is pierced by a number of small holes and wrapped in several turns of fine copper gauze, led to the establishment of this as a standard preparative method. It appears that the gauze not only acts thermally by rapidly conducting heat away from 'hot' spots, but also exerts a catalytic effect.

With ethane and fluorine in the molecular proportion of 1:6, yields of up to 80% of C_2F_6 were obtained; but considerable dilution of the fluorine with nitrogen was necessary before substantial quantities of the intermediate partly fluorinated compounds could be isolated. The best results were obtained[14] with $F_2:C_2H_6:N_2 = 4:1:2$ when 90% of partially fluorinated products was obtained.

Extension of this method to the fluorination of methane[15] gave, with $F_2:CH_4:N_2 = 2:1:10$, up to 45% of products of b.p. higher than that of CF_4, but the latter compound could be exclusively produced by increasing the concentration of fluorine and diminishing that of nitrogen. Some of the products obtained by Bigelow and his colleagues are shown in Table I (see page 200).

Cady[20] made the process more effective by packing the reaction vessel with silvered copper turnings which allowed a higher reaction temperature (up to 300°) to be used; this prevents decomposition of polymers on the catalyst with consequent loss of activity. Other workers[21] have found advantages in the use of gold-plated copper catalysts.

3. FLUORINATION WITH HIGHER INORGANIC FLUORIDES

This method, often called 'Fowler's method' after the leader of the team who first investigated it,[23] consists in the use of a fluoride – originally CoF_3, though CeF_4, MnF_3 and AgF_2 can also be used – as fluorinating agent.[13] In the original method cobalt trifluoride was prepared by dehydrating cobalt chloride by heating this salt spread on trays in a nickel reaction vessel, converting the anhydrous chloride to the difluoride by heating in a stream of anhydrous hydrofluoric acid at 400°, and then reducing the temperature to 250–300° and forming the trifluoride with elementary fluorine. Silver difluoride is prepared in a similar manner. After purging free fluorine from the apparatus with nitrogen the fluorides are allowed to react with the organic materials.[24] It will be noted that although free fluorine is not used in the final fluorination it is essential for the preparation of the active agent; hence the method is rather expensive and is often used for completing fluorinations which have been carried to a certain point by hydrogen fluoride in the presence of catalysts (see page 210). Various improvements have been made in the design of the

TABLE I. - PRODUCTS OBTAINED BY DIRECT FLUORINATION

Parent Substance		Product	m.p.°C.	b.p.°C.
Ethyl Chloride[16]	CF_4	Carbon tetrafluoride	-186 ± 1	-130 ± 1
	CF_3Cl	Chlorotrifluoromethane	-181 ± 2	-80
	CF_3CF_2Cl	Chloropentafluoroethane	-106	-38
	CHF_2CH_2Cl	2-Chloro-1, 1-difluoroethane	-	+35
	$CF_2 = CCl_2$	1, 1-Dichloro-2, 2-difluoroethylene	-116	0
	C_2F_6	Perfluoroethane	-	-78
Acetone[17]	CF_3COCF_3*	Perfluoroacetone	-129	-28
	COF_2	Carbonyl fluoride	-114	-83
	$(COF)_2$	Oxalyl fluoride	-	+26
	CH_2FCOCH_3	Monofluoroacetone	-	+78
Benzene[18]	CF_4, C_2F_6	(See above)		
	C_3F_8	Perfluoropropane	-	-38
	C_4F_{10}	Perfluorobutane	-	- 5
	C_5F_{10}	Perfluoro*cyclo*pentane	-	+ 1
	C_5F_{12}	Perfluoropentane	-	+22
	C_6F_{12}†	Perfluoro*cyclo*hexane	+48- 9	+52
	C_6HF_{11}	Undecafluoro*cyclo*hexane	-	+62
	$C_{12}F_{22}$	?	+19 -21	+90/90 mm.
Hexachloro-benzene[19]		A variety of unidentified products including $C_6Cl_6F_6$.		

* Soluble in water and giving a semicarbazone.

† Has a liquid range of only 3 -4°.

reactor,[21,25] and a 90% conversion of a hydrocarbon to the perfluoro compound can be attained (calculated on fluorine taken from CoF_3). The cobalt difluoride remaining after the reaction can be re-converted to the trifluoride many times before replacement is necessary. Silver difluoride is frequently preferred for liquid phase fluorination since the residual cobalt difluoride is very bulky whereas silver fluoride is granular and more easily separated from the product.

TABLE II. - PERFLUOROCARBONS OBTAINED WITH CoF_3

Parent	Product		Boiling range (°C.)	Yield %
		Perfluoro		
Pentane	C_5F_{12}	-pentane	82·4-82·6	86
*cyclo*Pentane	C_5F_{10}	-*cyclo*pentane	23·5-23·7	60
Dimethyl*cyclo*pentane	C_7F_{14}	-dimethyl*cyclo*pentane	71·5-71·8	46
Ethyl*cyclo*pentane	C_7F_{14}	-ethyl*cyclo*pentane	75·1-75·2	87
Benzotrifluoride	C_7F_{14}	-methyl*cyclo*hexane	76·3-76·4	88
Heptane	C_7F_{16}	-heptane	82·4-82·6	75
o-Xylene	C_8F_{16}	-*o*-dimethyl*cyclo*hexane	102·1-102·4	67
m-Xylene	C_8F_{16}	-*m*-dimethyl*cyclo*hexane	101·7-101·9	75
p-Xylene	C_8F_{16}	-*p*-dimethyl*cyclo*hexane	100·5-100·6	77
Bis(trifluoromethyl)benzene	C_8F_{16}	-*p*-dimethyl*cyclo*hexane	101·0-101·8	86
Mesitylene	C_9F_{18}	-1,3,5-trimethyl*cyclo*hexane	124·7-125·1	50
Indan	C_9F_{16}	-hexahydroindan	117·2-117·5	47
Hexadecane	$C_{16}F_{34}$	-hexadecane	238-240	73
Diphenyl ether	$C_{12}F_{22}O$	-di*cyclo*hexyl ether	175-176	47

In Table II is shown a series of typical products prepared by this method[22] together with their boiling ranges and the yields obtained (see page 200). McBee and Bechtol have extended this method to polycyclic hydrocarbons, using silver difluoride,[26] and some of their products are listed with their physical properties in Table III.

TABLE III. - SOME PERFLUORO FUSED-RING COMPOUNDS

Starting material	Product	b.p. °C.	f.p. °C.	d_4^{20}	n_D^{20}
	Perfluoro				
Napthalene	$C_{10}F_{18}$ -decalin	140	-7 to -10	1·9456	1·3118
1-Methylnaphthalene	$C_{11}F_{20}$ -1-methyldecalin	161	< -75	1·9606	1·3168
2-Methylnaphthalene	$C_{11}F_{20}$ -2-methyldecalin	160-1	< -60	1·9632	1·3164
Acenaphthene	$C_{12}F_{20}$ -perhydroacenaphthene	173	-2 to 0	1·9883	1·3292
Indan	C_9F_{16}, -hexahydroindan	116-7	-8 to -15	1·8838	1·3033
Fluorene	$C_{13}F_{22}$ -perhydrofluorene	190	< -40	1·9819	1·3264
Dimethylnaphthalene	$C_{12}F_{22}$ -dimethyldecalin	177-9	-30 to -40	1·9759	1·3200
Phenanthrene	$C_{14}F_{24}$ -perhydrophenanthrene	205-6	< -40	2·0197	1·3315
Anthracene	$C_{14}F_{24}$ -perhydroanthracene	211-2	+76-81	–	–
Fluoranthene	$C_{14}F_{26}$ -perhydrofluoranthene	235-9	-30 to -36	2·0598	1·3460

Attempts,[27] using AgF_2, to obtain perfluoro compounds from highly chlorinated terphenyl, triphenylene and 1,3,5-triphenylbenzene, gave compounds which still retained 20% of halogen as chlorine and belong to the fluorohalocarbon series; similar results were obtained with antimony pentafluoride. It is interesting to note that in 4-phenoxydiphenyl, dinaphthylene oxide, dibenzanthrone, triphenylamine and N-phenylcarbazole, the oxygen and nitrogen survive chlorination and fluorination.

All the compounds obtained by direct fluorination from aromatic or fused-ring hydrocarbons are fully saturated; none preserve an aromatic character, since the energy of addition of fluorine to the aromatic nucleus appears to be much less than that of substitution. If aromatic perfluoro compounds such as perfluorobenzene, C_6F_6, or perfluorotoluene, C_7F_8, are required a roundabout method must be used.[28] The most usual method of preparing such products is to fluorinate hexachlorobenzene with 3 moles of bromine trifluoride to give a

TABLE IV. - AROMATIC PERFLUORO- AND FLUOROHALO- COMPOUNDS

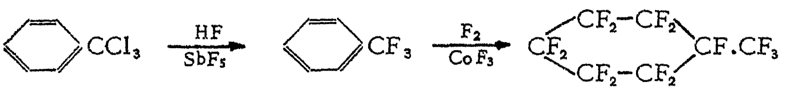
$C_nCl_aF_b$			b.p.		m.p.	n_D^{20}	d_4^{25}
n	a	b	°C.	at mm.	°C.		
	From Benzene						
6	–	6	81-2	743	-13 to -11	1·3760	1·612
6	–	8	56-57	743	+6	1·3149	1·601
6	1	5	122-3	750	–	1·4256	1·568
6	1	7	88-9	740	-60 to -65	1·3560	1·633
6	2	6	119-20	750	-25 to -30	1·4030	1·656
6	3	5	156-7	750	0 to +5	1·4466	1·692
6	2	8	112·5-3·5	750	-70°	1·3748	1·719
6	3	7	145·5	750	< -70°	1·4013	1·774
	From Toluene*						
7	–	8	103·5	740	< -70°	1·3664	1·660
7	1	7	135·8-6	740	< -70°	1·4043	1·700
7	2	6	170·5-0·7	742	-59 to -58	1·4445	1·715
7	2	10	128·5-9·5	750	< -70°	1·3681	1·759
7	5	9	158-160	745	< -70°	1·393	1·792

*All toluene derivatives contain the CF_3 group.

fluorohalocarbon having approximately the composition $C_6BrCl_4F_7$; on reduction with zinc dust in ethanol or acetamide, this compound gives the products shown in the upper part of Table IV (see page 201). Corresponding products from toluene are shown in the lower part of the same table.

4. FLUORINATION WITH ANHYDROUS HYDROFLUORIC ACID

Each of the methods previously described for preparing fluorocarbons involves the direct or indirect use of elementary fluorine. This is both expensive and inconvenient and in many cases can be either obviated or minimised by an exchange reaction with anhydrous hydrofluoric acid in the presence of a carrier catalyst. An additional advantage of such methods lies in the fact that no fragmentation of the carbon skeleton takes place. The main disadvantage is that the process seldom goes to the stage of complete fluorination even though compounds rich in fluorine are obtained. The latter can, however, be brought to the perfluoro stage by a subsequent treatment with fluorine, thus saving much of the expense of full fluorination with the element, with the further advantage that the direct perfluorination of a structure already containing a substantial proportion of fluorine is a more easily controlled reaction than the direct action of the element on the corresponding hydrocarbon. For example the conversion of benzotrichloride to perfluoromethyl*cyclo*hexane by the two stages



is cheaper and more easily controlled and also gives a higher yield of pure product than does the direct fluorination of toluene.[22]

By using anhydrous hydrofluoric acid under pressure with a little antimony pentafluoride as catalyst, carbon tetrachloride can be progressively converted into CCl_3F, CCl_2F_2, $CClF_3$ and CF_4: in general it appears that any compound containing the $-CCl_3$ group reacts readily under the conditions set out above to give the $-CF_3$ group; hence chloroform readily gives trifluoromethane and benzotrichloride gives benzotrifluoride. On the other hand the $-CHCl_2$ group reacts with some reluctance, usually giving $-CHClF$, and being converted to $-CHF_2$ only under very severe conditions, while $-CH_2Cl$ and $-CHCl$ are scarcely affected.[29] A review of the application of this method with a complete list of aliphatic perfluoro compounds so prepared has been given.[29] The method is not applicable to the formation of aromatic perfluoro compounds,[77] but holds for chlorinated side-chains in such compounds. In such cases, *e.g.* bis-*m*- or bis-p- trichloromethylbenzene (from *m*- or p- xylene) where the chlorine is very reactive,[30,31] a 50% conversion to the bis-trifluoromethyl compound takes place in anhydrous hydrofluoric acid containing 5% of SbF_5. This approach to the $-CF_3$ compounds has been used industrially.[32-36] Perfluoroheptanes and (*n*)polychloro (16–*n*) polyfluoroheptanes have been produced by analogous methods.[37-39]

5. ELECTROCHEMICAL FLUORINATION

The most remarkable advances in perfluorination have been made in the last few years with the aid of Simons' electrochemical process.[40] This process entirely avoids the preparation of elementary fluorine by dissolving or suspending the substance to be perfluorinated in anhydrous hydrofluoric acid and using the solution, with some potassium fluoride, as an electrolyte. Nickel anodes and steel cathodes are used with a potential difference of 5–6V.

The success of the process depends largely on the fact that perfluoro compounds are insoluble both in the parent hydrocarbons and in hydrofluoric acid, and so either separate immediately from the electrolyte as liquids or solids, or, if volatile, may be condensed from the effluent gases of the cell. This method is of almost universal application and has made available an enormous number of perfluorocompounds and fluorocarbons. Hydrocarbons usually yield the corresponding perfluoro compounds; acids and alcohols yield more complex mixtures of which the main constituents are usually the analogous perfluoro hydrocarbon with the same number of carbon atoms; at the same time some incompletely perfluorinated structures are obtained. Perfluoro compounds in which elements other than carbon and fluorine are present can also be prepared in this way (see page 211).

UNSATURATED ACYCLIC FLUOROCARBONS

Special interest attaches to the unsaturated acyclic fluorocarbons in view of their polymerization to analogues of polyethylene which have outstandingly resistant properties. The most commonly encountered member of this series is perfluoroethylene $CF_2{=}CF_2$ made in large quantities for the production of Fluon (Teflon). It is obtained by non-catalytic pyrolysis[41] of one of the Freons – chlorodifluoromethane – in polished silver tubes at 600 – 660°, $2CHClF_2 \rightarrow CF_2{=}CF_2 + 2HCl$; the yield is 90% or better, and the high-boiling fraction, which has been accumulated and examined in detail, consists of fluorohalocarbons of formula $H(CF_2)_nCl$, together with some cyclic compounds of interest.

TABLE V. - CONSTITUENTS OF HIGH-BOILING FRACTION FORMED IN $CHClF_2$ PYROLYSIS

Compound: $H(CF_2)_nCl$

Values of n	2*	3⁑	4	5	6	7	8	9	10	11	12	13	14
b.p.°C.	-10	+21	50	77	100	122·5	144·5	162·5	177	191	202	213	227-8
m.p.°C.	-	-	-	-	-	-	-	-	46	52	78	87	95
d_4^{20}	-	1·556	1·607	1·661	1·719	1·738	1·778	-	-	-	-	-	-
n_D^{20}	-	1·29	1·30	1·30	1·3012	1·3070	1·3088	-	-	-	-	-	-

Compound: *cyclo* $(CF_2)_n$

Values of n	3	4	5
b.p.°C.	-29	-5	+20·5
m.p.°C.	-	-40	+7

Compound: $\begin{matrix}CF\\ \|\\ CF\end{matrix}\!\!>\!(CF_2)_n$

	2	3
b.p.°C.	+5	33-35
m.p.°C.	-	-

* About 20% in high-boiling fraction.

⁑ About 30% in high-boiling fraction.

Table V shows the compounds isolated and their physical properties. The identity of the open-chain compounds was checked by chlorination to the αω-dichloro compounds, $Cl(CF_2)_nCl$, some of which were known, and these in turn were fluorinated to the perfluoro hydrocarbon, $F(CF_2)_nF$, the properties of which had previously been recorded.

Tetrafluoroethylene is an odourless and colourless gas b.p. -76·3°C., f.p. -102°. It must be stored away from materials containing oxygen and in the presence of stabilisers such as tri-*tert.*-butylamine or pinene.[1] Chlorotrifluoroethylene (perfluorovinyl chloride), $CF_2{=}CFCl$, is also valuable as a substance giving industrially useful polymers. It is readily prepared by running the Freon $CF_2Cl{\cdot}CFCl_2$ into a boiling suspension of zinc-dust in ethanol; the vapours are passed through a column in which ethanol condenses and is returned to the reaction vessel, while chlorotrifluoroethylene – a gas, b.p. -27·8°C. – passes on and is condensed by refrigeration and pressure.[42] All possible fluorochloro derivatives of ethylene are known, and some of their boiling points are shown in Table VI; it will be seen that the boiling point falls by about 50°C. for each chlorine atom replaced by fluorine.[43]

TABLE VI. - BOILING POINTS OF CHLOROFLUOROETHYLENES

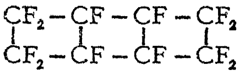
$CF_mCl_{2-m}CF_nCl_{2-n}$	m n 2 2	m n 2 1	m n 1 1	m n 1 0	m n 0 0	m n 2 0
b.p. °C.	-76·3	-28	+21	+71	+121	ca. 20

The dichlorodifluoroethylene, CFCl=CFCl, is the raw material for producing perfluorobutadiene, also valuable for its polymers. When *sym*-dichlorodifluoroethylene is subjected to the action of fluorine at -20° it is largely (40%) converted into 1,2,3,4-tetrachlorohexafluorobutane:-

$$2CFCl{=}CFCl + F_2 \rightarrow CClF_2{\cdot}CClF{\cdot}CClF{\cdot}CClF_2$$

$$CClF_2{\cdot}CClF{\cdot}CClF{\cdot}CClF_2 \xrightarrow[EtOH]{Zn} CF_2 = CF{\cdot}CF = CF_2.$$

This, on dechlorination with zinc and ethanol,[44] yields hexafluorobutadiene. An alternative method of preparing perfluorobutadiene is from $CF_2{=}CFCl$ which dimerizes at 600° to $CF_2{=}CF{\cdot}CFCl{\cdot}CF_2Cl$ which may be dechlorinated to perfluorobutadiene with zinc and ethanol. It is a reactive liquid, b.p. 7°C., which not only yields long chain polymers, but also on non-catalytic polymerization at 200° gives a dimer C_8F_{12}, a remarkable saturated fluorocarbon, m.p. 40°C., b.p. 80°, for which the following structure has been suggested:



Only a few highly fluorinated compounds containing the triple bond have been prepared. Haszeldine[45] obtained the trifluoropropyne, $CF_3{\cdot}C{\equiv}CH$, as a colourless gas, b.p. -48·3°C.; it is intensely reactive in the normal triple bond manner and has a smell resembling that of acetylene. It is concluded, therefore, that the proximity of a $-CF_3$ group does not interfere seriously with the acetylenic function provided one hydrogen atom remains; on the other hand Henne and Finnegan[46] prepared perfluoro-2-butyne ($CF_3{\cdot}C{\equiv}C{\cdot}CF_3$), in which no hydrogen remains, and found it to be a colourless liquid, b.p. -24·7° to -24·5°C. of very sluggish reactivity; it could, however, be oxidized easily to perfluoroacetic acid, and reduced by hydrogen and Raney nickel progressively to $CF_3{\cdot}CH{=}CH{\cdot}CF_3$ and $CF_3{\cdot}CH_2{\cdot}CH_2{\cdot}CF_3$.

PHYSICAL PROPERTIES OF FLUOROCARBONS AND FLUOROHALOCARBONS

The boiling points of perfluorohydrocarbons in the C_1-C_4 range are somewhat higher than those of the corresponding hydrocarbon,[47] but from C_4 onwards the fluorocarbon has the lower boiling point, the divergence increasing with the carbon number (see Table VII, page 206). The greatest regularity in boiling points appears in the perfluorohydroaromatic fused ring series where the approximate relation exists $t_f = t_h - 5n$ where t_f is the b.p. of the perfluoro compound, t_h that of the perhydro compound and n the carbon number.

In general, melting points, except for those of carbon tetrafluoride and perfluoropropane, are higher than those of the corresponding hydrocarbons, owing, presumably, to the higher atomic mass of fluorine as compared with hydrogen. (See Table VIII). The m.p. of perfluoro*cyclo*hexane is very near its b.p., figures of +50°C. and +52°C. respectively having been given for these quantities,[48] although other authors[1] show the m.p. 58°C. (sealed tube) to be higher than the b.p. 51°C.

The densities of fluorocarbons are roughly twice those of the corresponding hydrocarbons and the temperature coefficients of change of density are much higher than for any other common substance.[48] This leads to the rapid establishment of turbulence on heating which in association with the other physical and chemical properties of fluorocarbons, particularly low surface tension, great stability and lack of corrosive action, makes them ideal heat-transfer liquids.

VISCOSITY OF FLUOROCARBONS

The viscosity of fluorocarbons is higher than that of the corresponding hydrocarbons; some examples[47] are shown in Table IX, from which it is clear that the viscosity is maintained at higher temperatures by the higher fluorocarbons in such a way as to make them useful as lubricants. The fact that most fluorocarbons are stable indefinitely at 300°C. and many show no breakdown at even higher temperatures makes them valuable as high-temperature lubricants.

TABLE VII. - SOME PHYSICAL PROPERTIES OF FLUOROCARBONS

Substance		b.p. °C.	b.p. °C. parent hydrocarbon	Δ °C.	m.p. °C.	d/t°C.	$n_D^{t^{\circ}}$
PARAFFINS (normal chain) C_nF_{2n+2}							
CF_4	$n = 1$	−128	−161	−33	−184	1·96/−184°	—
C_2F_6	2	−79	−89	−10	−100·6	1·85/−78°	—
C_3F_8	3	−38	−44	−6	−183	1·45/0·2°	—
C_4F_{10}	4	−5	−0·5	+4·5	glass	1·47/20°	—
C_5F_{12}	5	+22	+36	14	—	—	—
C_6F_{14}	6	51	69	13	—	—	—
C_7F_{16}	7	82	98	16	−55	$1{\cdot}801-0{\cdot}00240t_{0-60}$	1·2770▲
C_8F_{18}	8	103·3	125	22	−65	$1{\cdot}839-0{\cdot}00251t_{0-60}$	1·2820▲
C_9F_{20}	9	125·3	151	26	−16	$1{\cdot}860-0{\cdot}00248t_{0-60}$	1·2865▲
$C_{10}F_{22}$	10*	144·2	174	30	+36	$1{\cdot}873-0{\cdot}00230t_{35-60}$	1·2890▲
$C_{11}F_{24}$	11*	161	196	35	57	$1{\cdot}919-0{\cdot}00248t_{60-130}$	1·2960▲
$C_{12}F_{26}$	12*	178	214	36	75	$1{\cdot}961-0{\cdot}00256t_{80-175}$	—
$C_{16}F_{34}$	16*	232	287	55	125	—	—
UNSATURATED ACYCLIC							
	$CF_2{=}CF_2$	−76·3	−103	−26·7	−142·5	1·616/−100° 1·368/−40°	—
C_4F_6	$CF_2{=}CF{\cdot}CF{=}CF_2$ (monomer)	+6·6	+1	−5·6	—	—	—
$(C_4F_6)_2$	$CF_2{=}CF{\cdot}CF{=}CF_2$ (α-dimer)	98−100	—	—	—	—	—
$(C_4F_6)_2$	$CF_2{-}CF{\cdot}CF{=}CF_2$ (β-dimer)	—	—	—	+40	—	—
C_4F_6	$CF_3.C{\equiv}C{\cdot}CF_3$	−24·5	27	+51·5	—	—	—

* All substances thus marked are white crystalline solids; all others are colourless gases or liquids.

▲ −0·00040t

TABLE VII. - SOME PHYSICAL PROPERTIES OF FLUOROCARBONS Continued

Substance		b.p. °C.	b.p.°C. parent hydrocarbon	Δ °C.	m.p. °C.	d/t°C.	$n_D^{t°}$
BRANCHED ACYCLIC Perfluoro-							
C_4F_{10}	-*iso*butane	+3	-10	-13	—	—	—
C_7F_{16}	-2,2,3-trimethylbutane	82·2	—	—	-80	1·7535/30°	1·2676/30°
C_8F_{18}	-2,2,4-trimethylpentane	104	—	—	—	1·8002/30°	1·2733/30°
Cyclo ALKANES Perfluoro-							
C_4F_6	-*cyclo*butene	+1	+2	+1	-60·4	—	—
C_4F_8	-*cyclo*butane	-5	12	17	—	—	—
C_5F_{10}	-*cyclo*pentane	+20·5	50·5	30	-12	1·64/30°	1·24/30°
C_6F_{12}	-*cyclo*hexane*	52	81	29	+50†	1·684/30°	1·2685/30°
C_7F_{14}	-methyl-*cyclo*hexane	76·2	100	24	-37	1·7779/30°	1·2762/30°
C_8F_{16}	-1,3-dimethyl-*cyclo*hexane	101·5	121	19·5	-55	1·8270/30°	1·2858/30°
C_9F_{18}	-1,3,5-trimethyl-*cyclo*hexane	124·6	140	15	-56	1·8676/30°	1·2930/30°
PERFLUOROAROMATIC COMPOUNDS Perfluoro-							
C_6F_6	-benzene	81-82	80·2	~1	~-12	1·612	1·376
C_7F_8	-toluene	103·5	110·8	7·3	<-70	1·660	1·3664
PERFLUORO HYDROAROMATIC FUSED RING COMPOUNDS Perfluoro-perhydro-							
C_9F_{16}	-indene	116-117	163	46	-8 to -15	1·8838/20°	1·3033/20°
$C_{10}F_{18}$	-naphthalene	141·9	188	46	-7 to -10	1·9456/20°	1·3118/20°
$C_{11}F_{20}$	-1-methyl naphthalene	161	210	49	<-75	1·9606/20°	1·3168/20°
$C_{11}F_{20}$	-2-methyl naphthalene	160-1	211	50	<-60	1·9632/20°	1·3164/20°
$C_{12}F_{22}$	-diphenyl*	—	—	—	+75	—	—
$C_{12}F_{20}$	-acenaphthene	173	235-6	62	-2 to 0	1·9883/20°	1·3292/20°
$C_{13}F_{22}$	-fluorene	190	253-8	~65	<-40	1·9819/20°	1·3264/20°
$C_{14}F_{24}$	-anthracene*	211-3	272-7	~65	+76 to 81	—	—
$C_{14}F_{24}$	-phenanthrene	205-6	270-5	~65	<-40	2·0197/20°	1·3315/20°
$C_{16}F_{26}$	-fluoranthene	235-9	—	—	-30 to -36	2·0598/20°	1·3460/20°
$C_{18}F_{32}$	-retene	~135/10mm.	—	—	—	2·05/30°	1·343/25°
$C_{18}F_{30}$	-chrysene	~135/10mm.	—	—	—	2·06/25°	1·344/25°

* All substances thus marked are white crystalline solids; all others are colourless gases or liquids.

† Has a liquid existence of only 2 or 3 degrees.

TABLE VIII. - COMPARISON OF MELTING POINTS OF FLUOROCARBONS AND HYDROCARBONS[48]

	m.p.°C. Hydrocarbon	m.p.°C. Fluorocarbon	Δ°C.
Methane	−183	−184	−1
Ethane	−172	−100·6	+71
Propane	−187·1	−183	+4
Heptane	−90·6	−78	+13
Hexadecane	+18·13	+115	+97
*cyclo*Pentane	−93·3	−12	+81
*cyclo*Hexane	+6·5	+50	+43
Bi*cyclo*hexyl	+20	+75	+55

TABLE IX. - VISCOSITIES OF SOME FLUOROCARBONS

Paraffin fluorocarbons C_nF_{2n+2}	Viscosity (in millipoises) at									
	25°	30°	35°	45°	60°	70°	80°	85°	90°	100°
$n =$ 7	9·15	8·31	7·69	6·61	–	–	–	–	–	–
8	14·9	13·6	12·4	10·4	8·12	7·07	–	–	–	–
9	18·1	16·3	14·7	12·2	9·15	–	–	–	–	–
10	–	–	20·5	16·4	12·0	10·0	8·37	–	–	–
11	–	–	–	–	16·4	13·5	11·1	–	9·38	–
12	–	–	–	–	–	–	13·1	11·9	10·8	10·0

The direct polymerization of tetrafluoroethylene or chlorotrifluoroethylene gives solid polymers of higher molecular weight than is desired for lubricant oils; the ideal perfluoro lubricant would be a mixture probably of average molecular weight ~10,000, corresponding to a chain length of about 20 carbon atoms, with a boiling range of 150–200°C. at 10 mm. and suitable viscosity. The polymerization of chlorotrifluoromethane can be controlled by the use of suitable peroxide concentrations in the chloroform solutions:-

$$CHCl_3 + n(CF_2{=}CFCl) \rightarrow Cl_3C(CF_2CFCl)_nH$$

In this reaction the growing chain molecule reacts with chloroform and chain growth ceases; thus the compound formed contains chlorine in excess of that contributed by the monomer. These 'polymer oils' are not stable until they have been fluorinated.[50] In Table X are shown the viscosities of polymer oil fractions; in the lower part of the Table the corresponding properties of the fluorinated polymer oils are given.[42]

Despite the fact that these mixed polymers do not retain their viscosity at higher temperatures quite so well as the fluorocarbons, they are shown to have, under practical conditions, lubricating properties at least equivalent to those of ordinary lubricants, in addition to their thermal stability.

The length of the polymer chain in C_2F_4 polymerization can be controlled to give lubricating oils and greases[51] by carrying out the polymerization in the presence of iodine which stops the growth of the chain at $n = 8-15$:-

$$I_2 + nC_2F_4 \rightarrow I(C_2F_4)_nI$$

Cobalt fluoride fluorination of the mixed polymers replaces the iodine by fluorine and gives a product which may be fractionated to give fluorocarbon oils and greases; these have been termed industrially 'Fluorolubes'. A typical 'Fluorolube' has the specification:-

Colour	Water-white
Acidity	Nil.
Water (Max. %)	0·005
V.P. at 140°F. (Max.)	$8{\cdot}0 \times 10^{-2}$
Viscosity in centipoises at 210°F.	25·0
Stability	Inert to CoF_3 at 200°C.

TABLE X. - VISCOSITY OF POLYMER OIL FRACTIONS (AS PREPARED AND FLUORINATED)

Fraction range °C.		Viscosity (centistokes) 100°F.	210°F.
POLYMER OIL	100–110	22·9	2·88
	110–120	59·4	4·73
	120–130	104	6·19
	130–140	185	8·20
	140–160	403	13·0
FLUORINATED POLYMER OIL			
	127–137	32·2	2·73
	137–147	75·7	4·1
	147–157	249	6·1

Another method of preparing fluorocarbons of this class is to take advantage of the reaction of Prins[52–54] in which carbon tetrachloride and trichloroethylene yield *sym.*-heptachloropropane and to polymerize fluorohalocarbons in its presence;[55] as with chloroform the chain-growth stops at 6–20 carbon atoms and the product may be perfluorinated to yield a satisfactory lubricant.

The surface tension of perfluoro compounds is the lowest observed among all organic substances:[47] for example perfluoro-octanoic acid (prepared by the electrochemical method from octanoic acid solutions in anhydrous hydrofluoric acid) in 0·3% solution reduces the surface tension of water from 72·8 to 16 dynes/cm.;[56] whereas the most powerful commercial surface-active agents produce a lowering to only 27–30 dynes/cm.

The atomic parachor of fluorine in fluorocarbons is 22·6, taking 8·6 for carbon.[57]

Fluorocarbons are insoluble in water, and most are insoluble also in anhydrous hydrofluoric acid; some are soluble in halocarbons and most fluorocarbons are miscible one with another forming very stubborn azeotropes;[58] fluorocarbons are insoluble in hydrocarbons - a mixture of heptane, perfluoroheptane and water separates into three immiscible layers.

CHEMICAL PROPERTIES OF SATURATED FLUOROCARBONS

Saturated fluorocarbons are characterized by chemical inertness;[59] they are unaffected by all common reagents at all strengths and at temperatures up to 400°C. They will yield up their halogen[60] to fused potassium at 500–550°C. or to sodium in liquid ammonia,[61] but appear to undergo practically no other chemical reactions excepting pyrolytic decomposition at temperatures of 500–1000°C. (when the products are mainly smaller fluorocarbons) and combustion in fluorine.

POLYMERS OF UNSATURATED FLUOROCARBONS

The tendency to polymerize shown by unsaturated hydrocarbons persists in their perfluoro analogues. This has been much studied in connexion with perfluoroethylene, chlorotrifluoroethylene and perfluorobutadiene, all of which produce polymers of high chemical resistance and excellent electrical properties.

POLYPERFLUOROETHYLENE, (FLUON, TEFLON)

This polymer, first[62] prepared in 1939, has proved to be of immense value technically. It is obtained by the simple process of treating an agitated aqueous suspension of benzoyl peroxide with C_2F_4 under pressure.[63] The polymer separates as a dense, white, crystalline powder which needs only washing and drying. As so prepared it has great stability but no mechanical cohesion; it is quite unchanged by heating at 300-310°C. for long periods, but at 327°C. it undergoes a transition to a tough translucent massive form. Unfortunately, it does not undergo viscous flow[64] so that it is lacking in one of the major qualities of a 'plastic'. This lack of flow means that the formation of articles in the polymer must be achieved by machining the rough shapes obtained by compressing the powder above 327°C. in a suitable mould. Numerous patents have been directed to the preparation and working of this polymer,[65-69] and attempts have been made, not without some success, to obviate the mechanical disadvantages of polyperfluoroethylene by co-polymerization with ethylene,[70] vinyl chloride or fluoride[71] or *N*-alkoxymethylpolyamides;[72] a detailed discussion of this problem is, however, outside the scope of this work.

POLY(CHLOROTRIFLUOROETHYLENE)

The problem of obtaining a somewhat more tractable isomer has also been approached by polymerizing chlorotrifluoroethylene, giving Keflon (or Kel-F), having chemical properties only slightly inferior to those of polyperfluoroethylene and, moreover, being more easily shaped and worked. On pyrolysis at 450-475°C. this polymer depolymerizes giving the monomer and a quantity of dichlorohexafluoro*cyclo*butane.[73]

POLYPERFLUOROBUTADIENE

This substance might be expected to show elastic properties, but the course of polymerization of hexafluorobutadiene is abnormal. The products are shown in Table XI and are liquids.[44]

TABLE XI. - PRODUCTS OF POLYMERIZATION OF PERFLUOROBUTADIENE

Product	Polymerization conditions (°C.)			
	44hrs. at 150°	5hrs. at 160°	18hrs. at 180°	44hrs. at 180°
Hexafluoro*cyclo*butene	6·5	5·4	14	14
Dimer (high-boiling)	66	88	39	33
Dimer (low-boiling)	—	—	2·25	5·1
Trimer	17	3·3	31·5	34
High-boiling residue	1·5	0·35	4	6

The electrical properties of the C_2F_4 and C_2F_3Cl polymers are very good; Fluon (Teflon) has a dielectric constant (ϵ) of 2·1/25° (compared with benzene, 2·29; chloroform 5·2 and ethanol 26·8) while the dissipation factor is <0·0005 at $60-10^{10}$ cycles. The fact that arcing or sparking does not decompose these materials to form carbon makes them virtually 'non-tracking'. These properties are surpassed by those of perfluorotri-*n*-butylamine $(C_4F_9)_3N$ which in addition to being completely inert and non-basic has a dielectric constant 1·85 at 25°C./100 cycles and a dissipation factor of 0·0005 up to 10 megacycles.

PERFLUORO COMPOUNDS WITH ELEMENTS ADDITIONAL TO CARBON

The most commonly encountered members of this series are the fluorohalocarbons, especially those in which the other halogen is chlorine. The origin of the modern development was in the recommendation of Henne and Midgeley in 1930[74] of dichlorodifluoromethane as a practical refrigerant. Their search for a non-toxic, non-corrosive, non-inflammable liquid having the desired thermodynamic properties led them to examine CCl_2F_2 which proved the ideal solution to their problem. This substance, named 'Freon', was the forerunner of a whole family of chlorofluoromethanes all now called Freons in the United States of America, ('Arctons' in the United Kingdom and 'Frigènes' in Germany) the original substance being distinguished as 'Freon 12'. The members of the group are chiefly the fluoro and chlorofluoro derivatives of methane, ethane and propane, and a number of them are shown, with their properties, in Table XII. Both Freon 12 and Freon 13 behave well as insulators, but their vapours can be broken down by persistent high tension discharge to carbon tetrachloride, carbon tetrafluoride and traces of free chlorine.[75]

TABLE XII. - SOME CHLOROFLUOROMETHANES AND ETHANES

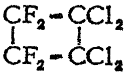
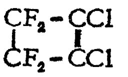
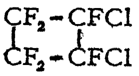
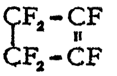
Formula	Name	m.p.°C.	b.p.°C.	Ref.
$CHFCl_2$	Chlorofluoromethane	–	+9	1
CHF_2Cl	Chlorodifluoromethane	–	-41	1
CHF_3	Trifluoromethane	–	-82	15
$CFCl_3$ (Freon 11)	Trichlorofluoromethane	-111	+25	8
CF_2Cl_2 (Freon 12)	Dichlorodifluoromethane	-169	-29	8
CF_3Cl (Freon 13)	Chlorotrifluoromethane	-181	-80	8
CF_3CHCl_2	1,1-Dichloro-2,2,2-trifluoroethane	–	-7	1
$CFCl_2CFCl_2$	1,1,2,2-Tetrachlorodifluoroethane	+28	+91	15
CHF_2CH_2F	1,1,2-Trifluoroethane	-84	+3	14
CHF_2CHF_2	1,1,2,2-Tetrafluoroethane	–	-22 to -23	14
CF_3CHF_2	Pentafluoroethane	-103	-48·5	14
CF_3CF_2Cl	Chloropentafluoroethane	-106	-38	16

The majority of these substances can be prepared from chloroform, carbon tetrachloride or a chlorinated derivative of ethane or ethylene by catalytic fluorination with anhydrous hydrofluoric acid in the presence of a carrier such as SbF_5, $SbCl_5$, CoO_3, MnF_3 etc. The choice of a refrigerant rests on three factors: availability, b.p., and high fluorine content. The high fluorine content is to ensure absence of toxicity and corrosive action, and the choice of b.p. depends on the duty to be performed by the refrigerator. Commercial refrigerators, where temperatures of -12 to -22° are necessary, use substances such as Freon 12 (CCl_2F_2, b.p. -29°C.); for domestic refrigerators, where temperatures need not fall below -10°C. a Freon boiling between -10° and 0°C. will serve equally well; with the higher boiling compound less pressure will be developed and so a lighter and cheaper construction can be used.

The effect of isomerism among fluorohalocarbons is shown most markedly in the m.p.; thus Haszeldine and Sharpe[1] have drawn attention to the physical properties of the four pentachlorotrifluoropropanes:-

	b.p.°C.	m.p.°C.	n_D^{20}
$CFCl_2.CF_2.CCl_3$	154·5	<-80	1·4394
$CF_2Cl.CCl_2.CFCl_2$	152·3	-4·9	1·4396
$CF_2Cl.CFCl.CCl_3$	153·3	-14·8	1·4392
$CF_3.CCl_2.CCl_3$	153·1	+109	–

The refractive indices of the three liquid isomers are almost identical and all four isomers boil within a range of 2·2°C., but the melting points differ widely. Studies[76 77] of the dimerization of 1,1-dichloro-2,2-difluoroethylene ($CF_2{=}CCl_2$) and chlorotrifluoroethylene led to the recognition of the differences between these substances and trifluoroethylene, the latter forming 'top to tail' polymers, and the former dimers such as 1,1,2,2-tetrachlorotetrafluoro*cyclo*butane; the four substances obtainable are:-

	b.p. °C.	m.p. °C.	$d^{4}_{t^{\circ}}$	n^{t}_{D}
	131·6/762 mm.	84·8	–	–
	67·1/61·5 mm.	-43·4	1·5340/25°	1·3699/25°
	59·87/760 mm.	-24	1·6441/20°	1·3340/20°
	1·13	-60·37	–	–

PERFLUORO COMPOUNDS CONTAINING OXYGEN

Acetone[17] has been perfluorinated directly with elementary fluorine to $CF_3.CO.CF_3$, a colourless liquid, b.p. -28°C., m.p. -129°. Like acetone it is soluble in water, and readily gives the semicarbazone (m.p. 153°, with 1 H_2O). During the preparation of perfluoroacetone,[78] both COF_2 ('fluorophosgene') b.p. -83° (previously examined by Ruff[78]) and trifluoroacetyl fluoride, CF_3COF, b.p. -59°, were obtained.[79] Analogous compounds have been obtained from methyl ethyl ketone and *cyclo*pentanone ($CF_3.CO.C_2F_5$ and C_5F_8O), whilst it has been shown that the CO groups in such structures as dibenzanthrone survive perfluorination.[27] The cobalt trifluoride method, however, cannot be used for the perfluorination of simple ketones.

Both carbon monoxide and methanol, on direct fluorination,[89] yield trifluoromethyl hypofluorite, CF_3OF, b.p. -94·2 ± 0·5°C. This substance is an analogue of CCl_3SCl; thus it cannot be reduced to perfluoromethanol, CF_3OH, but gives fluorophosgene:

$$CF_3OF + H_2 \rightarrow COF_2 + 2HF.$$

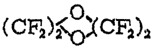
The substance is stable to heat up to 450°, passing through a copper tube heated to that temperature without change.[80] It is slowly decomposed by water.

Ethers have been perfluorinated, and perfluorodi*cyclo*hexyl ether has already been described (page 200). The electrochemical method has been found satisfactory for the preparation of difluoroethers[81] and they may be also prepared by direct fluorination.[1] The boiling points of some perfluoro ethers are shown in Table XIII and Haszeldine[1] has pointed out that with the exception of the initial member of the series - perfluorodimethyl ether - these constants are almost identical with those of the perfluorohydrocarbons of the same carbon-number. They are similarly inert.

Numerous perfluoro acids have been obtained, and in many cases the electrochemical method is very sucessful, leading to both the perfluoro acid, *e.g.* $CF_3(CF_2)_nCOOH$, and to its acid fluoride, $CF_3(CF_2)_nCOF$, from which the acid itself can be obtained.

Haszeldine[82-83] synthesized perfluoro acids through trifluoroiodomethane which has a labile iodine atom: it is prepared from the silver or lead salt of

TABLE XIII. - PERFLUOROETHERS

Formula	Name	b.p. °C.	b.p.°C. of hydrocarbon of same carbon number.
$(CF_3)_2O$	Perfluorodimethyl ether	−59	−79
$(C_2F_5)_2O$	Perfluorodiethyl ether	+1	−0·5
$(C_3F_7)_2O$	Perfluorodipropyl ether	56	51
$(C_4F_9)_2O$	Perfluorodibutyl ether	101	103
$(C_5F_{11})_2O$	Perfluorodiamyl ether	139	144
$C_4F_9OCF_3$	Perfluorobutylmethyl ether	35·4	—
	Perfluorodioxan	13	–
$(C_2F_5OCF_2CF_2)_2O$	Perfluorodiethoxydiethyl ether	96·6	—

trifluoroacetic acid and iodine. With tetrafluoroethylene, it reacts to form heptafluoro-1-iodopropane in which the iodine is still labile and will react with acetylene to give heptafluoro-1-iodopentene; this, when oxidized with permanganate yields perfluorobutyric acid,[83] C_3F_7COOH, b.p. 120·8–121°C., n_D^{16}, 1·295.

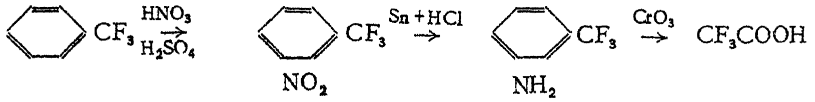
$$CF_3COOAg + I_2 \rightarrow CF_3I + CO_2 + AgI$$

$$CF_3I + C_2F_4 \rightarrow CF_3.CF_2.CF_2I \xrightarrow{C_2H_2}$$

$$CF_3CF_2CF_2CH{=}CHI \xrightarrow{KMnO_4} CF_3CF_2CF_2COOH$$

Aqueous solutions of the perfluoro acids have remarkably low surface tensions (see page 208).

Trifluoroacetic acid, CF_3COOH, is an interesting case of a compound, already known for some time in small quantities, which has recently been produced on a large scale. The ready availability of benzotrifluoride and the great stability of the CF_3 group make this the best source of trifluoroacetic acid. Nitrated benzotrifluoride is reduced to 3-aminobenzotrifluoride which on oxidation with chromic acid yields trifluoroacetic acid:[84]

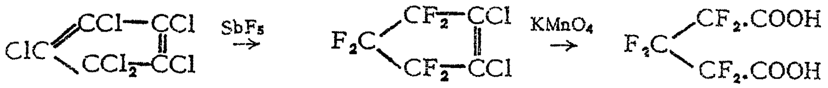


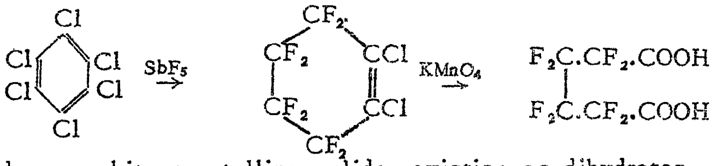
This compound may also be prepared from acetic acid by electrochemical fluorination, by the fluorination of acetone over nickel shot,[85] or by alkaline permanganate oxidation of certain unsaturated fluorohalocarbons, for example $CF_3.CCl{=}CCl_2$ or $CF_3.CCl{=}CCl.CF_3$. The acid, b.p. 72°, is extremely strong, fuming in air, stable in aqueous solution and readily yielding salts. Its anhydride, $(CF_3.CO)_2O$, is a valuable esterifying agent:[86]

$$\text{alcohol} + \text{acid} + (CF_3.CO)_2O \rightarrow \text{ester} + 2CF_3COOH$$

Perfluorobenzoic acid, C_6F_5COOH, m.p. 106–7°, has been prepared by refluxing perfluorotoluene with excess of concentrated sulphuric acid for one week, with vigorous stirring:[87] $C_6F_5.CF_3 \rightarrow C_6F_5COOH$.

Several of the perfluorodibasic acids are known. Perfluorosuccinic acid, $(CF_2COOH)_2$ m.p. 86·4–87·4°C., b.p. 150°C./15mm., was obtained by permanganate oxidation of either 1,2-dichloro-3,3,4,4-tetrafluoro*cyclo*butene or perfluoro*cyclo*butene.[88] Similar procedures have been used to obtain perfluoroglutaric acid and perfluoroadipic acid starting from perchloro*cyclo*pentadiene and perchlorobenzene respectively:[89]





The two acids are white crystalline solids, existing as dihydrates. Their chemical reactions are normal, and esters, amides and nitriles can be prepared from them by ordinary reactions.[89]

CARBONYL FLUORIDE (FLUOROPHOSGENE) COF_2

Humiston in 1919[90] attempted to prepare carbonyl fluoride by passing carbonyl chloride and fluorine over heated calcium fluoride in a glass tube; condensation of the product indicated an apparent b.p. of -42°, from which it appears that the substance was carbonyl chlorofluoride, COClF, later prepared by Emeléus and Wood[91] by the action of antimony pentafluoride on carbonyl chloride and shown to have b.p. $-45{\cdot}0 \pm 0{\cdot}2$°C. Carbonyl chlorofluoride has also been obtained[92] from carbonyl chloride and AsF_3, although this reaction does give substantial amounts of carbonyl fluoride. Ruff and his co-workers,[93] observing that the interaction of carbon monoxide with fluorine gave only impure products, obtained carbonyl fluoride from silver difluoride and carbon monoxide; $CO + 2AgF_2 \rightarrow COF_2 + 2AgF$. They report m.p. $-114 \pm 0{\cdot}3$°C., b.p. $-83{\cdot}1 \pm 0{\cdot}5$°C., $d = 1{\cdot}809 - 0{\cdot}00420T$, heat of evaporation 3842 g.-cal./mole, and Trouton's constant 20·3. Carbonyl fluoride has also been observed as a product of the arc discharge in a mixture of CF_4 and CO[94] and as a by-product in the fluorination of acetone;[17, 95] it is formed by passing dichlorodifluoromethane[96] over heated tungsten dioxide at 525°, and by the action of iodine on sodium trifluoroacetate where it appears as a minor constituent of the decomposition products.[97] It does not seem to be formed[98] from carbonyl chloride and anhydrous hydrofluoric acid, but has been obtained in substantial yield,[91] from carbonyl chloride reacting with slight excess of antimony trifluoride in the presence of a little antimony pentafluoride in an autoclave at 200 - 280°C. for 12 hours.

The equilibrium $CO + F_2 \rightleftharpoons COF_2$ has been studied, and the reaction has been shown to proceed to the left at high temperatures;[99] the effect of catalysts at 300-1200°C. led to the conclusion[100] that COF_2 has a negative heat of decomposition of ~26 g.-cal.

The heat of formation has been given[101] as:-

$$F_2 + C\,(\text{diamond}) + \tfrac{1}{2}O_2 = COF_2 + 142 \pm 1\ \text{kg.-cal.},$$

or

$$F_2 + CO = COF_2 + 115\ \text{kg.-cal.};$$

later the same authors[102] gave $150{\cdot}35 \pm 0{\cdot}5$ kg.-cal. for the first of these heats of formation. The infra-red and Raman spectra have been plotted[103] with the following results:-

Infra-red bands (gas) cm.$^{-1}$	**4120v.w.**	**3882w.**	**3696v.w.**	**3403v.w.**	**3163v.w.**	**2887w.**	**2682v.w.**
	2472w.	**1941*v.s.**	**1249v.s.**	**965*s.**	**775*s.**	**626*m.s.**	**584*m.s.**
Raman lines (liquid) cm.$^{-1}$	**1944v.w.**	**1909m.**	**1238v.w.**	**965s.**	**771v.w.**	**620m.**	**571w.**

*** fundamental vibrations.**

v.s. = very strong; s. = strong; m. = moderate; w. = weak.

These results indicate a planar model similar to that of $COCl_2$ and COH_2. Nielsen[104] has studied the rotational fine structure of the 775 cm^{-1} band.

PERFLUORINATED NITROGEN COMPOUNDS

Numerous perfluorinated amines are known[105,106] together with a few representatives of the perfluorinated heterocyclic series;[107,108] chemically they are very inert, and even when the nitrogen also carries a fluorine atom (as in perfluorodimethylamine) they are stable to aqueous alkali. The majority of the compounds of this series are prepared by direct fluorination of the dry amine, or by the use of cobalt trifluoride. Some of their properties are shown in Table XIV.

TABLE XIV. - SOME PERFLUORO AMINES

Formula	Name: Perfluoro	b.p.°C.	n_D^{25}	d_4^{25}
$(CF_3)_3N$	-trimethylamine	-7 to -6		
$(CF_3)_2C_2F_5N$	-dimethylethylamine	20-22		
$CF_3(C_2F_5)_2N$	-methyldiethylamine	45·5-46·5		
$(C_2F_5)_3N$	-triethylamine	70·3	1·262	1·736
$(C_3F_7)_3N$	-tripropylamine	129·9	1·279	1·822
$(C_3F_7)_2(isoC_4F_9)N$	-dipropyl*iso*butylamine	146·8	1·283/5°	1·84/1°
$(C_4F_9)_3N$	-tributylamine	179·3	1·291	1·873
$(CF_3)_2NF$	-dimethylamine	-37		
CF_3NF_2	-methylamine	-75		
$C_5F_{10}NF$	-piperidine	+49		
$(CF_3)_2C_5F_8NF$	-2,6-dimethylpiperidine	m.p.94-5		
$C_6F_{11}NF_2$	-*cyclo*hexylamine	+76		

Trichloroacetonitrile heated with hydrochloric acid under pressure yields 2,4,6-tris(trichloromethyl)-1,3,5-triazine which can be fluorinated by anhydrous hydrofluoric acid in the presence of antimony pentachloride,[109] giving seven intermediate stages up to complete perfluorination. The properties of the compounds are shown in Table XV.

TABLE XV. - FULLY CHLORO/FLUORINATED 1,3,5-TRIMETHYLTRIAZINES

Formula	b.p.°C. (748 mm.)	f.p.°C.	n_D^{20}	d_4^{26}
$C_6N_3F_9$	98·3-98·5	-24·8	1·3231	1·5857
$C_6N_3F_8Cl$	119·0-119·2	-51·6	1·3540	1·6090
$C_6N_3F_7Cl_2$	145·1-145·3	-36·2	1·3827	1·6234
$C_6N_3F_6Cl_3$	166·6-166·8	-21·1	1·4129	1·6458
$C_6N_3F_5Cl_4$	194·2-194·4	-9·4	1·4420	1·6656
$C_6N_3F_4Cl_5$	217·0-217·2	-10·2	1·4611	1·6860
$C_6N_3F_3Cl_6$	248·1-248·3	+9·6	1·4920	1·7134
$C_6N_3F_2Cl_7$	274·5-274·7	14·0	1·5009	1·7400
$C_6N_3Cl_9$	—	96·0	—	—

Phosphorus[110] and arsenic react with trifluoroiodomethane to give the following compounds:-

	b.p.°C.		b.p.°C.
$P(CF_3)_3$	17·3	$As(CF_3)_3$	33·3
$P(CF_3)_2I$	73	$As(CF_3)_2I$	14/54mm.
$P(CF_3)I_2$	133/413mm.		

These substances lack the inert character of the perfluoro amines and the phosphorus compounds burn readily.

The substance CSF_2 has been reported,[109] but a single carbon and sulphur are more likely to take up eight fluorine atoms to form $CF_3.SF_5$ which may quite readily be prepared by the cobalt fluoride reaction on methyl thiol,

$$CH_3SH + 6F_2 \rightarrow CF_3.SF_5 + 4HF,$$

or by the direct action of fluorine diluted with nitrogen on the same substance.[111] The product, thiocarbonyl octafluoride, is a colourless gas, chemically inert but decomposed by sodium at a dull red heat. It has m.p. $-86{\cdot}9 \pm 0{\cdot}2$°C.; b.p. $-20{\cdot}4$°C., and has a transition point at $-153 \pm 0{\cdot}3$°C. It is a good electrical insulator in the gas phase but breaks down on sparking. The relative insulating values of air, dichlorodifluoromethane and thiocarbonyl octafluoride have been assessed[112] as 1:2:3.

Several valuable reviews dealing with the perfluoro compounds have been compiled.[113-123]

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SECTION IX.

SPECTROSCOPY OF FLUORINE, HALOGEN FLUORIDES, HYDROGEN FLUORIDE AND FLUORINE OXIDES.

By R. F. BARROW

THE FLUORINE ATOM.

OPTICAL SPECTRA

A number of investigators have contributed to the analyses of the atomic spectra of fluorine. A list of the more important experimental work, roughly in order of increasing excitation, is given below, the investigations which have led to the determinations of ionization potential being indicated (I.P.).

Reference		Spectrum	λλ, A.	Notes
Gale	1	I	3470–7800	
Gale and Monk	2	I	3400–7000	also F_2 bands
Carragan	3	I	6239–7573	Zeeman effect
Dingle	4	I	6239–7800	I.P.
Dingle	5	I	7654–8300	I.P.
Bowen	6	I–IV	419–958	
de Bruin	7	I, II	3057–4447	I.P.
Edlén	8	I–III	214–743 950–960 2397–3156	 I.P.
Edlén	9	I	6047–9433	
Lidén	10	I	5500–6500	Stark effect
Lidén	11	I	5538–7110	
Dingle	12	II	1700–8347	I.P.
Bowen	13	II–IV	125–620	I.P.
Dingle	14	III	2206–3268	I.P.
Edlén	15	IV, V	140–680 2170–3176	I.P.
Edlén	16	I–VII	86–1139	Summary of wave-lengths
Edlén	16	IV–VI	2170–4593	analysis V, VI
Edlén	17	V	119–1090 2450–2704	
Edlén	18	VI, VII	86–1139	
Tyrén	19	VIII	13–17	
Flemberg	20	VIII	13–17	I.P.
Finkelnberg	21	IX	–	I.P. (extrapolated)

The analyses of these spectra have been collected together by Moore,[22] whose tables also include the results of a great deal of unpublished work by Edlén. Summaries of wave-lengths are given by Edlén,[16] in the Multiplet Tables of Princeton University[23] for λ>3000 A. and of Moore[24] for λ<3000 A.

Hyperfine structure in the spectrum of FI has been studied by Campbell[25] who showed that the nuclear spin of F^{19} is $\frac{1}{2}(h/2\pi)$. Other properties of the F^{19} nucleus have been summarized by Meggers[26] (see also page 53).

The ground state of the F atom has the configuration $1s^2\ 2s^2\ 2p^5$, ^2P: the ^2P term is inverted, $^2P_{1/2}$ lying 404·0 cm.$^{-1}$ above $^2P_{3/2}$. There are no very low-lying states: values for the lowest states, taken from Moore[22] are as follows:-

$2s^2.2p^4.3s$	$^2P_{1/2}$	105057·10 cm.$^{-1}$
	$^2P_{3/2}$	104731·86
	$^4P_{1/2}$	102841·20
	$^4P_{3/2}$	102681·24
	$^4P_{5/2}$	102406·50
$2s^2.2p^5$	$^2P_{1/2}$	404.0
	$^2P_{3/2}$	0.0

All the ionization potentials of F are known. The values below are from Moore[22] with the exception of that for F IX which was derived by extrapolation.[21]

Initial state	I. P.	Initial state	I.P.
F I $^2P_{3/2}$	17·42 v.	F VI $^1S_0$	157·117 v.
F II $^3P_2$	34·98	F VII $^2S_{1/2}$	185·139
F III $^4S_{3/2}$	62·646	F VIII $^1S_0$	953·60
F IV $^3P_0$	87·23	F IX $^2S_{1/2}$	1102
F V $^2P_{1/2}$	114·214		

The relations of the ionization potentials to those of other elements have been considered.[27-31] The total electronic binding energy, Σ(I.P.), is 2714·3 eV., which may be compared with the value 2690·6 eV. calculated by Duncanson and Coulson.[32]

The *raies ultimes* were studied by de la Roche.[33] The M.I.T. tables[34] list the following lines:-

Wave-length, A.	6902·46	6856·02
Excitation potential, V.	14·5	14·4

The CaF bands are also excited very readily in some sources.[35]

Apart from the work considered above, which is mainly experimental, there have been a number of studies of theoretical problems closely connected with the subject of spectroscopy of the F atom. Wave-functions for the the ground state of F I have been calculated by Brown[36] using the self-consistent field, and by Duncanson and Coulson,[37] who derived analytical functions using the variation principle. Self-consistent field wave-functions for the ground state of the F^- ion have been calculated by Brown[36] and by Hartree:[38] analytical functions are also given by Morse, Young and Hauritz,[39] some of whose work is, however, incorrect in detail.[37] Wave-functions and energies of a number of states of highly ionized fluorine have been computed. Morse et al.[39] considered F^{4+}, F^{5+}, F^{6+} and F^{7+}; Wu and Shen[40] derive the energies of a number of anomalous states in F^{5+} and F^{6+}; Goldberg and Clogston[41] treat states of F^{6+} and F^{7+}. The subject of the calculation of atomic wave-functions is reviewed by Hartree.[42]

A calculation[43] of the ground-state interval $^2P_{3/2} - {}^2P_{1/2}$ in F I based on Brown's wave-functions[36] yields −189 cm.$^{-1}$ as compared with the experimental value of −404 cm.$^{-1}$. Araki[44] has given an interpretation of the intervals in certain multiplets in F II and other spectra in which the coupling is Russell–Saunders but where the intervals do not obey the Landé rule: the anomaly is shown to arise from spin–spin interaction. The calculated energies of various levels[45] in $p^n.p$ and $p^n.d$ configurations[46] for F I, F II and F III are in reasonable agreement with experiment.

The absorption coefficient of atomic fluorine in the region of continuous absorption corresponding to the process $F + h\nu = F^+ + e^-$ for $h\nu$ in the range 13·6 to 24·6 x 10^4 cm.$^{-1}$ has been estimated.[47]

Refs. p. 220

X-RAY SPECTRA

Measurements of the K_{α} radiation have been made by a number of investigators.[48-54,19] Tyrén's measurements[19] are given below (A.):

Source	$K_{\alpha_{1,2}}$	$K_{\alpha'}$	K_{α_3}	K_{α_4}
NaF	18·318	18·268	18·219	18·190
MgF_2	18·324	18·274	18·233	18·198
CaF_2	18·325	18·269	18·225	18·196
AlF_3	18·303		18·225	18·192

The results for MgF_2 and CaF_2 are considered to be identical within the limits of experimental error, but the wave-lengths from NaF appear to be significantly lower. The effect of lattice binding on wave-lengths in the *K* series has also been considered by Sawada, Furuta and Kosugi.[55]

The wave-length of the *K*-edge was found[53] to be 17·91 A. A critical potential corresponding to the *L*-radiation at 195 A. was measured by Levi.[56] Methods of estimating *K*, *L* and *M* levels for the lighter elements have been considered.[57]

When monochromatic *X*-rays fall upon matter, there is scattered radiation not only of the same frequency as, but also of lower frequency than, that of the incident radiation: this is the Compton effect.[58,59] If the electrons responsible for the scattering were at rest, the Compton modified line would lie at a single frequency, determined by the angle between incident and scattered radiation. However, if the electrons are in motion, there is a Doppler effect, related to their velocities. Thus the modified Compton line becomes a band whose profile results from the momentum distribution among the scattering electrons.[60] The theoretical shape of the Compton profile has been calculated by Duncanson and Coulson,[61] who criticize earlier work.[62] Tables of atomic scattering factors have been published.[63]

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THE FLUORINE MOLECULE, F_2

The F_2 molecule shows no banded structure in absorption in the wavelength region so far examined. Continuous absorption at $\lambda < 4100$ A. was detected by Gale and Monk.[1] Quantitative studies[2] indicate that the absorption maximum is near 2900 A., or according to Bodenstein et al.[3] 2820 A. (see Fig. 1).

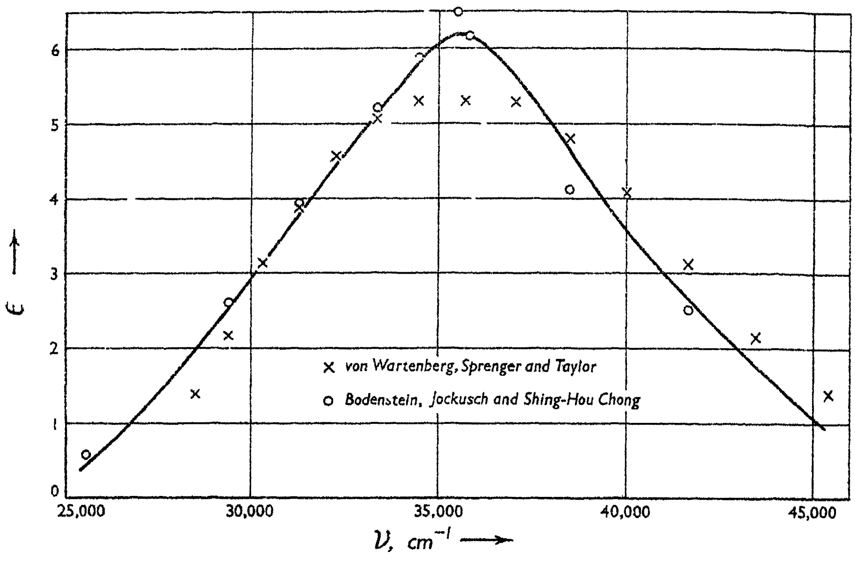

Fig. 1.

The absence of low-lying excited states of F_2 is suggested by the failure of Nathans[4] to obtain absorption bands in the region 7000 to 9600 A. The ultra-violet continuum arises from the transition $Q^1\Pi - X^1\Sigma_g^+$[5,6] transitions to $Q^3\Pi$ being unimportant, conclusions which are confirmed by calculations of the absolute intensity.[7,27] In particular the trend of increasing intensity in the direction F_2 to I_2 in these continua is well reproduced in the calculated values.

The lack of an accessible discrete electronic band-system involving the ground state of F_2 led to the difficult investigation of the Raman spectrum. Earlier attempts to observe the spectrum of the liquid failed,[8] but both the vibrational and the rotational effects have now been observed in F_2 gas.[9,10] The former leads to $\Delta G''_{1/2}$ (the interval between $v''=0$ and $v''=1$) $= 891{\cdot}8_5 \pm 0{\cdot}4$ cm.$^{-1}$: the latter gives $B''_0 = 0{\cdot}8828$ cm.$^{-1}$: $r''_0 = 1{\cdot}417_7 \pm 0{\cdot}001$ A., in good agreement with the less precise electron diffraction values (see page 49). The anharmonic constant, $x''_e\omega''_e$ is not known: comparison with the other diatomic halogens suggests that it is probably about 8 cm.$^{-1}$, giving $\omega_e \sim 908$ cm.$^{-1}$. The force constant, k''_0, is $4{\cdot}45 \times 10^5$ dyne.cm.$^{-1}$.

Emission bands ascribed to F_2 were observed in the spectra of discharges through F_2 gas by Smythe[11] and analysed by Gale and Monk[1,12] and by Aars.[13] The constants of the two states involved are:

State	T_e	ω_e	$x_e\omega_e$	r_e, A.
$C^1\Sigma$	$x + 20900$	977·4	140·6	1·475 (r_0)
$B^1\Pi$	x	1139·8	9·7	1·282

The $C^1\Sigma$ state is extensively perturbed and the constants given for it are of less than their usual significance. The branch-lines are of alternating intensity. Gale and Monk found the ratio of intensities to be $\gg 3$: Aars found values > 3. Doubtless the high values arise from the effects of perturbations. Andrychuk[10] found 2·8 from the rotational Raman effect, in reasonable agreement with the value 3 expected for a nuclear spin of $\frac{1}{2}$.[14,15] He also showed that the ^{19}F nucleus obeys Fermi statistics.

The electronic states of F_2 have been the subject of theoretical work by Mulliken,[5,6] whose calculations of the overlap integrals in the ground state[16] throw some light upon the unexpectedly large value of the internuclear distance and small value of the dissociation energy. Perturbation calculations on the electronic states starting from the separated atoms have also been made.[17] Excited states of F_2 have been treated by Mueller.[18]

A value for the dissociation energy of F_2 of 63 kg.-cal. was derived by von Wartenberg, Sprenger and Taylor[2] from empirical arguments based on the position of the absorption maximum in $Q^1\Pi - X^1\Sigma_g^+$. Their arguments were severely criticised by Mulliken.[19] No quantitative treatment of the distribution of intensity in this continuum has been offered, although rough calculations have been carried out,[17] and it is not therefore possible to draw any conclusions about the value of D_{F_2} from what is yet known about the spectrum of F_2 itself. The value $D_{F_2} \sim 38$ kg.-cal.mole^{-1} has now been established: the values derived from cycles involving $Cl^{20}F$ and the alkali metal halides[21] are in good agreement with direct measurements.[22,23] The bearing of the value of D_{F_2} on temperatures in the H_2-F_2 flame is considered by Altman and Farber.[24]

Thermodynamic properties of F and of F_2 have been calculated from spectroscopic data.[25] There is an unexplained discrepancy of about 3·3 e.u. between the statistical value for S°_{298} of F_2 (gas) and that obtained calorimetrically.[26]

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HALOGEN FLUORIDES

Information about the spectra of the halogen fluorides is for the most part of comparatively recent origin, and the newly-developed techniques of micro-wave spectroscopy have been applied most successfully to the elucidation of the structures of some of these molecules.

DIATOMIC HALOGEN FLUORIDES

Each of the diatomic fluorides, ClF, BrF and IF, possesses a band-system in the visible region of the spectrum which is thought to arise from the transition $A^3\Pi_{0^+}-X^1\Sigma^+$, X (or N) being the ground state. The ClF bands are known only in absorption;[1,2] the system of BrF has been studied both in absorption[3,4] and in emission in the Br_2–F_2 flame;[5,6] IF is known only from the emission spectrum of the I_2–F_2 flame.[5,6] The constants of these states are collected in Table II (see page 225). The upper states, $A^3\Pi_{0^+}$, are none of them very stable, and reliable convergence limits have been obtained for all three molecules. Predissociation below the convergence limit has been observed for ClF and BrF. Good values of the dissociation energies of these molecules can therefore be obtained provided that the atomic products of dissociation of the *A* states can be identified. Durie[6] suggests plausibly that the products are Cl,Br,I $(^2P_{1/2})$ + $F(^2P_{3/2})$, and the dissociation energies given in Table I are derived on this assumption. In the case of ClF, uncertainty about the products of dissociation of the state $A^3\Pi_{0^+}$ is relatively unimportant, for the difference in energy of the only likely pairs of products, $Cl(^2P_{1/2}) + F(^2P_{3/2})$ and $Cl(^2P_{3/2}) + F(^2P_{1/2})$ is only 1·4 kg.-cal. Thus the main source of error in the determination of D_{F_2} through the ClF cycle seems to reside in the determination of the heat of formation of ClF gas.[7]

TABLE I.- CONVERGENCE LIMITS AND ENERGIES OF DISSOCIATION

Molecule	Ref.	Limit, $cm.^{-1}$	Limit, kg.-cal.	Excitation energy, kg.-cal.	D_0'', kg.-cal.
ClF	1	21508	61·48	2·52	58·96
BrF	6	21190	60·57	10·53	50·04
IF	6	23570	67·37	21·72	45·65

Note slightly different values of the limits have been given for ClF[2] and for BrF.[3,4]

Comparison with other halogen halides, for example ICl, suggests that these molecules should possess a number of other band-systems in the visible and ultra-violet regions of the spectrum. Hitherto only one further system, of very weak absorption bands of BrF lying in the region 17500 to 19000 $cm.^{-1}$, has been reported.[4]

The Raman spectrum of ClF liquid[8] and the infra-red[8,9] and micro-wave[10] spectra of ClF gas have also been studied. The Raman spectrum at −120°C. excited by Hg 5460 A. showed a single unresolved line at 758 $cm.^{-1}$: the Raman lines for ClF gas should lie at 773·9 (^{35}ClF) and 766·6 $cm.^{-1}$ (^{37}ClF). Very precise values of the ground-state constants of ClF have been obtained from the infra-red[9] and micro-wave[10] studies. In the latter work, the transitions J 1−0 from $v'' = 0$ and $v'' = 1$ were identified for ^{35}ClF and ^{37}ClF, from which accurate values of the rotational constants were obtained. These constants were then used in the analysis of the fine structure of the 1−0 and 2−0 vibration-rotation bands to derive the ground-state vibrational constants. The analysis of the hyperfine structure of the pure rotation spectrum led to the determination of the quadrupole coupling constants, and the dipole moment was derived from observations of the Stark effect. This subject has been reviewed by Gordy,[11] Whiffen[12] and Wilson.[13]

BrF has also been investigated in the micro-wave region.[14] The lines $J\,1-0$ for $v'' = 0$ and $v'' = 1$ of ^{79}BrF and ^{81}BrF were measured, and values of the rotational constants and of the quadrupole coupling constants derived. The dipole moment was derived from observations of the Stark effect. As in the case of ClF, the value of the internuclear distance derived from the analysis of the bands of the $A-X$ system is in satisfactory agreement with the more precise micro-wave value.

TABLE II. - SPECTROSCOPIC CONSTANTS FOR THE DIATOMIC HALOGEN FLUORIDES

	ClF		BrF		IF	
Upper state: $A^3\Pi_{0+}$		Ref.		Ref.		Ref.
$\nu_{0,0}$ cm.$^{-1}$	18718	1	18495	6	18955	6
ν_e, cm.$^{-1}$	18956	1	18650	6	19054	6
ω_e, cm.$^{-1}$	313·48	1	365	6	412·5	6
$x_e\omega_e$ cm.$^{-1}$	2·217	1	6	6	3·8	6
r_e, Å.	1·92	1	2·17	4	–	
Ground state: $X^1\Sigma^+$						
ω_e cm.$^{-1}$	786·34 778·82	9 9	673	6	610	6
$x_e\omega_e$ cm.$^{-1}$	6·23 6·11	9 9	4	6	3	6
B_e, cm.$^{-1}$	0·51651 0·50699	10 10	0·35717 0·35545	14 14	(0·281)	
α_e cm.$^{-1}$	$4{\cdot}359\times10^{-3}$ $4{\cdot}335\times10^{-3}$	10 10	$5{\cdot}214\times10^{-3}$ $5{\cdot}177\times10^{-3}$	14 14	– –	
r_e, A.	1·6281	10	1·7556	14	$(1{\cdot}90_6)$	
k_e, dyne/cm.	$4{\cdot}48\times10^5$	9	$4{\cdot}10\times10^5$	6	$3{\cdot}64\times10^5$	6
D_0, kg.-cal./mole, 0°K.	$58{\cdot}9_6$	1	$50{\cdot}0_4$	6	$45{\cdot}6_5$	6
μ, debye	0·88	10	1·29	14	–	
eqQ, mc./sec.	-145·99 -114·92	10 10	+1089·0 + 909·2	14 14		

Notes: Upper states–

(1) The upper state constants for all three molecules are subject to some uncertainty, for the values of v' do not appear to be established beyond doubt.

(2) The values of $\nu_{0,0}$, ω_e and of $x_e\omega_e$ refer to ^{35}ClF and to the mean molecule ^{79,81}BrF: IF is of course isotopically pure.

(3) The vibrational levels in all three upper states converge more rapidly than can be represented by terms in ω_e and $x_e\omega_e$ only.

Ground states–

(4) When two figures are given, *e.g.* for B_e, ω_e, the upper one refers to the lighter isotopic molecule, the lower to the heavier.

(5) The values for IF in parentheses have been estimated, using the additivity of covalent radii, and including an electronegativity correction.[16]

General–

(6) Slightly different values for some of the constants are given for ClF[2] and for BrF.[3,4]

POLYATOMIC HALOGEN FLUORIDES

Spectroscopic work, of varying degrees of completeness, has been reported for the following polyatomic halogen fluorides: ClF_3, BrF_3, BrF_5, IF_5 and IF_7.

CHLORINE TRIFLUORIDE

The absorption spectrum of gaseous ClF_3 has been studied in the region 2000 to 8000 A.[17,18] (See Fig. 2).

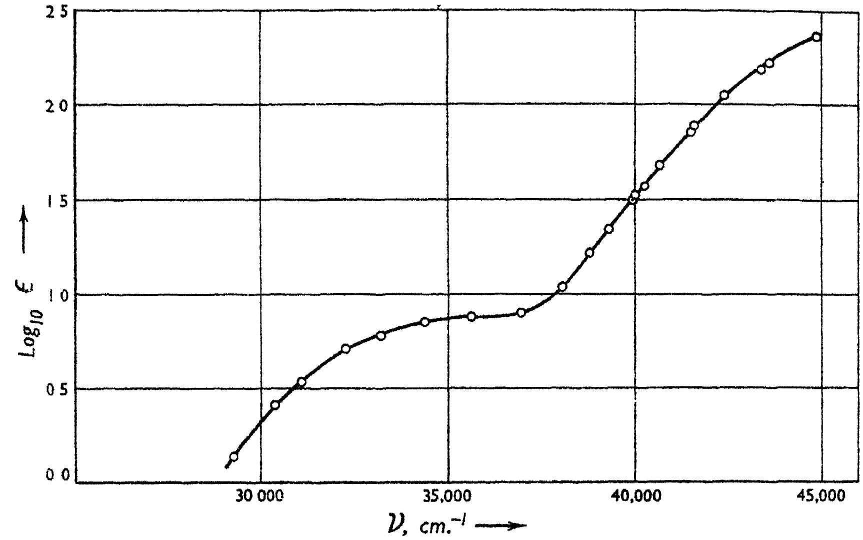

Fig. 2.

Absorption begins at about 4700 A., and slowly increases with decreasing wave-length until about 2600 A., when the rate of increase becomes more rapid. Neither maxima nor banded structure appear at $\lambda > 2200$ A.

The Raman spectrum of liquid ClF_3[19,20] proves to be more complex than was expected on the basis of presumed pyramidal or planar structures. there appear to be at least five Raman-active frequencies.[20] Similarly, no clear-cut results have yet emerged from the study of the infra-red spectrum of ClF_3 gas.[20] Suggested explanations of the anomalous Raman effect were: (i) that the molecule was less symmetrical than was supposed, (ii) that there is association in the liquid state. That (i), at least, is certainly true has now been shown by a determination by *X*-rays of the structure of crystalline ClF_3 at -120°C.[21] and by the analysis of the spectrum of ClF_3 gas in the micro-wave region.[22] The micro-wave spectrum is both weak and complex, and the first attempts at analysis failed. However the discovery that ClF_3 forms a molecular crystal, the ClF_3 molecules having the shape of a distorted T, provided the key to the analysis of the micro-wave spectrum which amply confirms the *X*-ray results. The molecule is planar, with a C_{2v} axis, and in the gas phase the dimensions are shown in Fig. 3 (see page 227). There is a unique Cl-F bond in ClF_3

What appear to be somewhat premature calculations of the thermodynamic properties of gaseous ClF_3 have been made:[19,23] this work has been criticised[24] on the grounds that it is based on an incorrect assignment of fundamental frequencies. The correct vibrational structure of ClF_3 has yet to be determined.

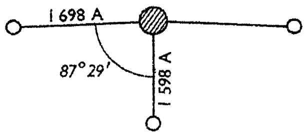

Fig. 3.

BROMINE TRIFLUORIDE

Qualitative observations on the absorption spectrum of BrF_3 gas in the ultra-violet region have been made.[25] Continuous absorption was first detected at $\lambda < 2800$ A. (See also page 159).

BROMINE PENTAFLUORIDE

The infra-red spectrum of BrF_5 gas and the Raman spectrum of the liquid have been studied.[26,27] From a consideration of the number of Raman-active and infra-red-active frequencies and of the polarization characteristics of the Raman lines it is concluded that the structure is that of a tetragonal pyramid (C_{4v}), with four fluorine atoms at the corners of the square base and the bromine and odd fluorine atoms on the four-fold axis normal to the base as shown in Fig. 4.

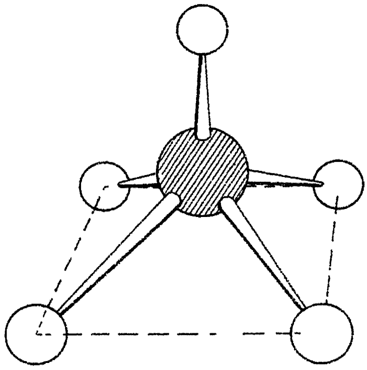

Fig. 4.

This structure is confirmed by the nuclear magnetic shielding experiments of Gutowsky and Hoffmann[28] which further indicate non-equivalent electron distributions in the structurally distinguishable bonds. A treatment of the force constants, and calculations of thermodynamic properties of gaseous BrF_5, following plausible assumptions about the molecular dimensions, have also been made.[27]

IODINE PENTAFLUORIDE

Qualitative observations on the absorption spectrum of IF_5 gas in the ultra-violet region have been made.[25] Continuous absorption was first detected at $\lambda \leqslant 2300$ A.

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The infra-red spectrum of IF$_5$ gas and the Raman spectrum of the liquid have been studied.[29] The results indicate that the structure is that of a tetragonal pyramid (C_{4v}) like that of BrF$_5$ shown in Fig. 4, and, as for BrF$_5$, this structure is confirmed by studies of nuclear magnetic shielding.[28] (See page 175).).

IODINE HEPTAFLUORIDE

The infra-red spectrum of IF$_7$ gas and the Raman spectrum of the liquid have been studied.[29] The structure of the molecule appears to be that of a pentagonal bipyramid (D_{5h}), as shown in Fig. 5.

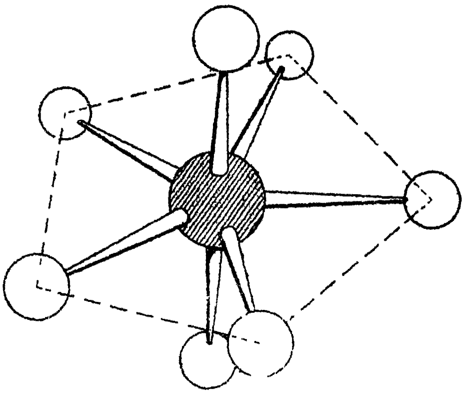

Fig. 5.

The iodine atom lies at the centre of a regular pentagon formed by five fluorine atoms and the two remaining fluorine atoms are equally spaced above and below the plane on the five-fold axis passing through the iodine atom. (See also page 179).).

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HYDROGEN FLUORIDE

INFRA-RED SPECTRA

Studies of the gaseous hydrogen halides played a most important part in the development of the spectroscopy of diatomic molecules in the decade 1920–30.[1] The lines J 2–1, 4–3, 5–4 in the rotation spectrum of HF were observed by Czerny[2] at 82·56, 163·44 and 204·94 cm^{-1} respectively. The fundamental vibration-rotation band of HF at 3963 cm^{-1} was resolved by Imes[3,4] and the first overtone at 7751 cm^{-1} was observed by Shaefer and Thomas.[5] The 3,0 and 4,0 bands were analysed by Kirkpatrick and Salant.[6] The 2,0, 3,0 and 4,0 bands of HF have since been examined under high dispersion by Naudé and Verleger,[7] and the 1,0 and 2,0 bands of HF and of DF by Telley, Kaylor and Neilsen,[8] who derive the following constants, taking into account the the measurements of Kirkpatrick and Salant.

$$\text{HF: } G_v = 4138{\cdot}52_2 u - 90{\cdot}06_9 u^2 + 0{\cdot}980 u^3 - 0{\cdot}025 u^4.$$

$$\text{DF: } G_v = 3000{\cdot}35_8 u - 47{\cdot}33_6 u^2 + 0{\cdot}373 u^3 - 0{\cdot}006_8 u^4.$$

$$\text{HF: } B_v = 20{\cdot}939_0 - 0{\cdot}770_5 u + 0{\cdot}005_0 u^2; \quad D_e = 0{\cdot}002_2.$$

$$\text{DF: } B_v = 11{\cdot}004_5 - 0{\cdot}293_6 u + 0{\cdot}001_4 u^2 \quad D_e = 0{\cdot}0006_5.$$

(In these equations, u is written for $v + \frac{1}{2}$: the constants are in cm^{-1}.)

$$r_e = 0{\cdot}9170_1\ \text{A}.$$

The results of the last three investigations[6-8] are in reasonable agreement, but the differences are such that too much weight should not be attached to the absolute values of coefficients of the higher powers of u.

As the pressure of hydrogen fluoride vapour is increased, bands ascribed to the effects of association appear on the long wave-length side of the monomer fundamental.[9] Shelton and Nielsen[10] find three distinct polymer bands at 3228, 3380 and 3497 cm^{-1}. The intensity of these bands varies steeply with the temperature: thus especially the 3380 and 3497 bands are considerably stronger at 52° than at 62°C. It is concluded that the polymers are few in number but that they absorb intensely. The suggestion is made that the three types of polymer band are associated with the three possible positions of a bond in a zig-zag chain polymer, thus:-

$$\text{F} \underset{1}{-} \text{H} \,.\,.\,.\,.\,.\, \text{F} \underset{3}{-} \text{H} \,.\,.\,.\,.\,.\, \text{F} \underset{2}{-} \text{H}$$

The infra-red spectrum of liquid or dissolved hydrogen fluoride differs from that of the gas and no rotational structure is observed.[9] The position of the 3,0 band in liquid hydrogen fluoride at the boiling-point is shifted about 1320 cm^{-1} to lower frequencies than in the gas.[11] In CCl_4 solution, the fundamental appears at 3860 as compared with 3963 cm^{-1} in the gas: the polymer bands are however absent.[9] Aqueous solutions of hydrogen fluoride give a band at 5·46μ not given by water alone, but so do a number of other acids, and the band is not characteristic of hydrogen fluoride.[12] The 9722 A. band of water is unaffected by the presence of up to 50% hydrogen fluoride.[11] An attempt to observe the Raman spectrum of a 40% aqueous solution of hydrogen fluoride failed because of a fluorescence.[13]

ULTRA-VIOLET SPECTRUM

Absorption first reported[14] in hydrogen fluoride in the region 1950 to 3200 A. was later shown to arise from sulphur dioxide present as an impurity.[15] Absorption in the pure gas begins at about 1650 A. at room temperature,[16,17] but as the temperature is raised the absorption shifts to longer wave-lengths, and spectra measured at 100° and at 165°C. (Fig. 6) show maxima at about 62000 cm.$^{-1}$ (1615 A.).

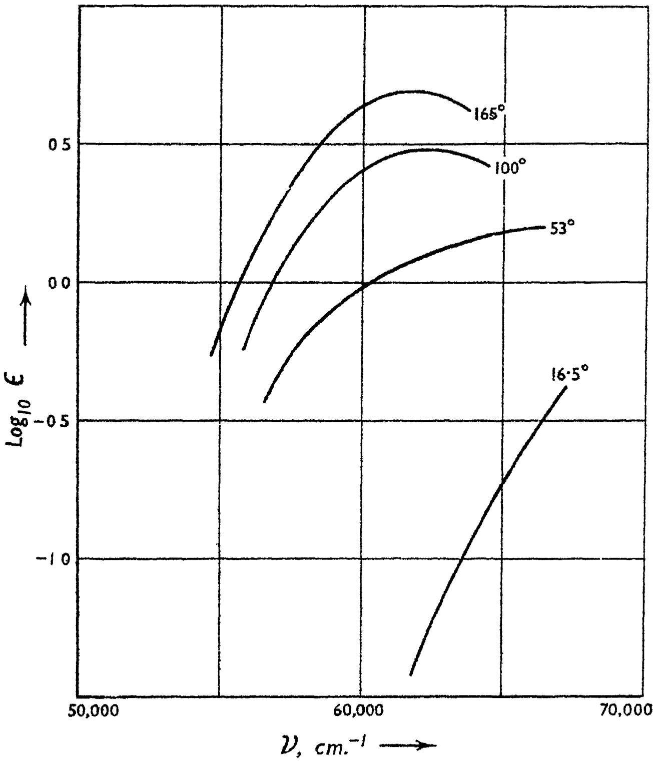

Fig. 6.

The interpretation of these results is not yet clear. No banded absorption has been observed down to 1500 A., the limit of the present observations. Liquid hydrogen fluoride has been found to be transparent at least down to 2200 A.

THEORY AND INTERPRETATION

Interpretations, made before the advent of wave-mechanics, of the infra-red spectra of HF have been given.[18-24] The calculation of molecular constants from the spectral data, using wave-mechanical formulae, was done for HF by Czerny.[25]

The intensities of overtone bands of HF has been calculated, using a Morse potential function, by Rosenthal[26] who derives the following values of the ratios of the integrated absorption coefficients $\alpha(v',0)/\alpha(1,0)$, 0·021, 0·0009, 0·00006 for $v' = 2,3$ and 4 respectively. (The Morse function gives the potential energy, $U(r)$, of a diatomic molecule in terms of two constants, D, the energy of dissociation, and $\beta = 1{\cdot}218 \times 10^7\ \omega_e(\mu_A/D)^{1/2}$ cm.$^{-1}$, where ω_e is the vibration frequency and μ_A is the reduced mass in atomic weight units. The function may be written $U(r) = D\{1-e^{-\beta(r-r_e)}\}^2$. Real molecules often follow

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the Morse potential quite closely, and it is convenient to use: thus the wave-equation is capable of exact solution for a Morse potential.[38-40])

Electron configurations in the states of HF have been considered in detail by Mulliken.[27,28] The predicted value[27] for the 'vertical' ionization potential (i.e. for ionization accomplished without change of internuclear distance) for $\sigma^2\pi^4,\ {}^1\Sigma^+ \longrightarrow \sigma^2\pi^3,\ {}^2\Pi$ is 18·23 eV. Mulliken has also calculated[28] the dipole strength of the $N \rightarrow Q(\sigma^2\bar{\pi}^4,\ {}^1\Sigma^+ \longrightarrow \sigma^2\bar{\pi}^3\sigma^*;\ {}^3\Pi, {}^1\Pi)$ transition. No comparison with experimental values[16,17] appears yet to have been made. The bond-moment in HF has been estimated by an ionic-covalent resonance treatment.[29] Hulbert and Hirschfelder[30] have calculated the potential curve for HF from experimental values of $\omega_e, x_e\omega_e, B_e, \alpha_e$ and of D_{HF}. Other potential functions have been tested by Davies.[41] The force-constant of HF has been considered in relation to those of similar bonds and to other bond-properties.[31-35] The question of the emissivity of gaseous HF, for example in high-pressure combustion chambers, has been considered by Penner.[36] Thermodynamic properties of gaseous HF have been calculated from the spectroscopic data.[37]

The dissociation energy of HF has not been determined with any accuracy from the study of its spectrum alone: it is best found from the heat of formation of HF and the values of D_{F_2} and of D_{H_2}. With $Q_f(\mathrm{HF}) = -64{\cdot}2$, $\tfrac{1}{2}D_{\mathrm{H}_2} = 52{\cdot}1$, $\tfrac{1}{2}D_{\mathrm{F}_2} = 19$, $D_{\mathrm{HF}}(298^\circ\mathrm{K.}) = 135{\cdot}_3$ kg.-cal./mole.

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THE HF^+ ION

Although band-systems of HCl^+ and HBr^+ are well-known, no system has yet been certainly attributed to the HF^+ molecule. Woods[1] in the course of experiments on CuF observed a many-line spectrum in the ultra-violet region which she tentatively ascribed to HF^+. What appears to be the same system was excited by Caunt and Barrow[2] in a hot hollow-cathode discharge containing KF or KHF_2 running in H_2. They analysed five bands of a $v' =$ constant progression: the molecular constants derived were such that the emitter could hardly be other than the hydride of an element in the first period of the periodic classification. The structure of the bands suggested that the transition is $^1\Sigma - {}^1\Sigma$, which would rule out HF^+; however, if spin-doubling effects were small, the system could be $^2\Sigma - {}^2\Sigma$ of HF^+.

That the states of HF^+ are unlike those of HCl^+ and HBr^+ follows from the fact that the ionization potential of F is greater than that of H, whereas those of Cl and Br are less. There may well be yet undiscovered bands of HF^+ in the red region of the spectrum.[3]

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THE FHF^- ION

Spectroscopic studies of crystalline KHF_2 have been of importance in determining the structure of the FHF^- ion. The absorption spectrum of single crystals in the infra-red was first examined by Buswell, Maycock and Rodebush.[1] More detailed work on KHF_2 and KDF_2 in absorption and in reflection was carried out by Ketelaar.[2,3] He showed that the bands obtained were truly to be associated with FHF^-, for the spectrum of KHF_2 is almost identical with that of $RbHF_2$ apart from a small shift to lower frequencies in the latter crystal. Moreover the spectrum of $K(90\%D, 10\%H)F_2$ is simply the sum of the spectra from FHF^- and FDF^-. However Ketelaar's frequency assignments were criticised by Pitzer and Westrum[4,5] who concluded, on the basis of a detailed review of thermodynamic and spectroscopic evidence, that the potential curve for the proton in the ion possesses only a single minimum. This conclusion has been confirmed by studies of the reflection spectrum of oriented single crystals measured in polarized light at room temperatures:[6] similar results but with improved resolution were obtained at −185°C. by Newman and Badger,[7] who list some 27 bands in the region 740 to 7326 cm.$^{-1}$ The values of the fundamental frequencies, cm.$^{-1}$, are:[6]

	reflection	absorption	
ν_2	1245	1222	(movement of proton perpendicular to the F − F line)
ν_2'	1250		
ν_3	1510	1450	(movement of proton along F − F line)

For KDF_2, $\nu_2 = 891$, $\nu_3 = 1046$ cm.$^{-1}$ (absorption).

The infra-red inactive frequency ν_1, corresponding to the symmetrical F − F vibration, has been found doubled at 595 and 604 cm.$^{-1}$ in the Raman spectrum of crystalline KHF_2.[8,9]

Confirmation that the structure of the FHF^- ion in crystalline KHF_2 is linear, with the proton half-way between the fluorines, has been obtained from neutron diffraction studies.[10,11]

No Raman effect was observed in concentrated aqueous solutions of KHF_2.[12]

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OXIDES OF FLUORINE

FLUORINE MONOXIDE, F_2O

The absorption spectrum of F_2O in the region 2100 to 8000 A. has been studied by Glissman and Schumacher.[1] They found continuous absorption, beginning at about 5400 A., with maxima at 4210, 3580, 2940 A., and at some undetermined wave-length less than 2100 A. (see Fig. 7). The compound gives fluorine and oxygen on photolysis.

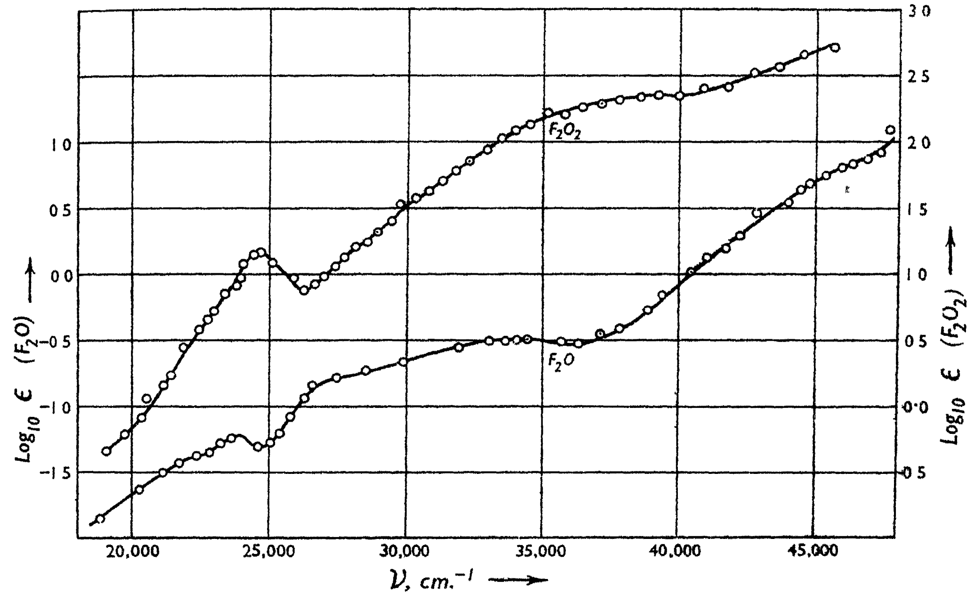

Fig. 7.

The vibration-rotation spectrum was first studied by Hettner, Pohlman and Schumacher,[2] who showed that the structure was that of an isosceles triangle with apex angle about 101°. However their assignment of fundamental frequencies was incorrect.[3,4] This spectrum has since been examined by Bernstein and Powling[5] and by Jones, Kirby-Smith, Woltz and Nielsen,[6] whose results are in quite close agreement.[7] All three fundamentals have been both observed and identified. From the fine structure of a perpendicular band, Bernstein and Powling derive $r(F-O) = 1{\cdot}38 \pm 0{\cdot}03$ A., $\angle FOF = 101{\cdot}5 \pm 1{\cdot}5°$, in satisfactory agreement with electron diffraction values (see page 191).

The relation between bond-distance and stretching force-constant has been considered by Gordy.[8] The potential function for F_2O has been considered by Duchesne and Burnelle[9] and by Linnett and Heath.[10] The latter conclude that repulsion between the fluorine atoms is significant and accounts for the major part of the deviation from the simple valency (or orbital) force field (for an account of the simple valency force field see, for example, Herzberg[11]). Thermodynamic properties of F_2O from 298 to 1500°K. have been calculated by Potter.[12] The probability of excitation of vibration and rotation of an idealized F_2O molecule by a neon atom has been the subject of a quantum-mechanical calculation by Aroeste.[13]

FLUORINE DIOXIDE, F_2O_2

The absorption spectrum of F_2O_2 has been examined in the region 2000 to 10000 A. by Brodersen, Frisch and Schumacher.[14] Absorption was first detected at about 5900 A. The extinction coefficient increases with decreasing wave-length, the maximum lying at some undetermined wave-length less than 2200 A. (See Fig. 7).

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SECTION X.

THE DETECTION AND ANALYTICAL DETERMINATION OF FLUORINE AND FLUORIDES.

By F. P. JOHNSON

DETECTION OF FREE FLUORINE

Free fluorine may be detected by its reaction with starch-iodide papers. The reaction is not specific, and should be supplemented by absorption in sodium hydroxide solution which is tested for fluoride ion.

DETECTION OF FLUORIDES

Alkali fluoride solutions give a precipitate of cerium fluoride CeF_3 with cerium nitrate in acetic acid solution.[1] Precipitates are also given by fluorides with lanthanum acetate[2] and with mercuric nitrate in nitric acid solution.[3] The test using the evolution of silicon tetrafluoride on warming with sulphuric acid and quartz sand may be made more sensitive by treating the silicic acid formed in the test with a drop of a nitric acid solution of ammonium molybdate, followed by the addition of an acetic acid solution of benzidine and a saturated solution of sodium acetate. A blue colour develops even when the amount of silica produced from the volatilised silicon tetrafluoride is as little as 0·0001 mg.[4] The red-violet colour of a solution of zirconium chloride in hydrochloric acid mixed with sodium alizarin sulphonate changes to yellow in the presence of fluorides because zirconium forms colourless complex anions $(ZrF_6)^{--}$; as little as 0·001 mg. of fluorine may thus be detected.[5] The brown insoluble zirconium compound, formed from zirconium salts and p-dimethylaminoazobenzenearsonic acid, reacts, with fluorides to produce the colourless ZnF_6^{--} ion and the free acid which is red in colour. This reaction may be carried out on impregnated papers.[6] Fluoride ions decrease the fluorescence given by morin with aluminium.[7] The yellow colour given by titanium compounds with hydrogen peroxide is bleached by fluorine ions through the formation of colourless H_2TiF_6.[8] A transient green flame coloration in obtained from a bead containing fluoride, potassium bisulphate and borosilicate, because of the production of volatile boron trifluoride.[9]

ANALYSIS OF FLUORINE GAS AND 'ACTIVE' FLUORINE COMPOUNDS

Fluorine may be determined by shaking with mercury in a special gas burette, the residual gases being transferred to ordinary gas analysis apparatus for the determination of carbon dioxide, oxygen, and inert constituents.[10] A method more suitable for industrial control removes hydrogen fluoride from the fluorine by absorption in sodium fluoride; the fluorine is then passed over sodium chloride, and the gas evolved is analysed for chlorine, oxygen and inert gases by standard procedures.[11] Fluorine in a mixture of gases liberates bromine from heated sodium bromide, and the bromine may be determined colorimetrically.[12]

'Available' fluorine in cobalt trifluoride may be determined by reaction with potassium iodide and titration of the liberated iodine with thiosulphate, or by reaction with excess of ferrous ammonium sulphate and back-titration with ceric sulphate.[13] Silver difluoride forms a eutectic mixture with silver iodide, which liberates iodine from acidulated potassium iodide. Alternatively silver difluoride may be reduced with hydrogen, the silver formed being weighed, and the liberated hydrogen fluoride determined by absorption in sodium hydroxide.[14]

DETERMINATION OF FLUORIDE

(a) GRAVIMETRICALLY

Several modifications have been suggested in the precipitation of calcium fluoride in the well known gravimetric method for the determination of fluorine, to facilitate filtration. Powdered calcium sulphate dihydrate, $CaSO_4,2H_2O$, may be used as precipitant, the increase in weight of the ignited mixed precipitate being determined after treatment with sulphuric acid.[15] Usually the calcium fluoride is precipitated together with calcium carbonate which is leached out with acetic acid prior to weighing. By using a membrane filter[16] or by precipitating in presence of a little ammonia[17] the co-precipitation with calcium carbonate may be avoided. Alternatively the calcium fluoride may be obtained in a readily filterable form by precipitation with calcium chloride in the presence of gelatin solution.[18]

Fluorides may be precipitated, with a solution of lead chloride, as lead chlorofluoride, $PbClF$, which may be filtered and weighed.[19] Rigid adherence to the proper conditions of precipitation is necessary. Triphenyltin fluoride is quantitatively precipitated from solutions of fluoride by triphenyltin chloride. Entrainment of excess reagent and washing difficulties in the presence of large amounts of foreign salts cause trouble with this method.[20] Other methods proposed are based on the precipitation of bismuth fluoride[21] or $[C_{12}H_8(NH_2)_2]_2,(HF)_4,HgF_2$, where $C_{12}H_8(NH_2)_2$ is the benzidine molecule.[22]

(b) VOLUMETRICALLY

Fluorine may be quantitatively separated as hydrofluosilicic acid, H_2SiF_6, by distilling with perchloric acid in a glass apparatus, water or steam being added to maintain the temperature at 135° during the distillation. The method is applicable to all fluorides soluble in perchloric acid, including materials such as cryolite, phosphate rock, fluorite, apatite etc. Some insoluble substances may require a preliminary fusion with sodium carbonate, while organic material such as foodstuffs must first be ashed in the presence of a fluorine fixative such as calcium oxide or magnesium oxide. The distillate is titrated with thorium nitrate solution using the coloured zirconium–alizarin complex as indicator.[23] In the original method the end point is indistinct, and it is greatly improved by using as indicator a solution of sodium alizarinsulphonate alone, which gives a pink colour with the excess thorium nitrate.[24] Interference by chloride, which distils over as hydrochloric acid, may be prevented by the addition of silver perchlorate to the distilling flask.[25] In the titration of large amounts of fluorine, the precipitate of thorium fluoride makes the detection of the end point difficult, and the formation of this precipitate may be prevented by adding starch solution.[26] After separating fluorine by distillation with perchloric acid, the distillate contains fluosilicate ions, and titration with thorium nitrate at pH 3, which is usual when using sodium alizarinsulphonate as indicator, may give low results. This error can be avoided by carrying out the titration at pH 5·3 with gallocyanine as indicator.[27] For the titration of very small amounts of fluoride, Solochrome Brilliant Blue BS[28] or Chrome Azurol S[29] are preferable as indicators.

As an alternative to weighing the precipitate of lead chlorofluoride, it is possible to dissolve the precipitate in nitric acid and to titrate the chloride by Volhard's method.[30] This volumetric method is more convenient than the gravimetric method, and usually gives more accurate results. A similar method utilizes the precipitation of lead bromofluoride when a known amount of potassium bromide, followed by lead acetate, is added to the fluoride solution. After filtration, the residual bromide in the filtrate is titrated, and hence the fluoride may be calculated.[31]

The formation and precipitation of cryolite, Na_3AlF_6, when aluminium chloride is added to a solution of a fluoride containing excess of sodium chloride has been used in several volumetric methods for the determination of fluoride. The end point of the titration may be detected by the hydrolysis of the excess aluminium chloride causing the neutral solution being titrated to become acid to methyl-red.[32] Alternatively, the excess aluminium at the end point may be detected by the formation of a red-violet lake with Eriochromecyanine R[33] or by the appearance of a fluorescence with morin.[34] Similarly, fluorides may be titrated with an alcoholic solution of ferric chloride, using ammonium thiocyanate as indicator, because the iron tends to form the FeF_6^{---} ion rather than undissociated FeCNS.[35] Other methods involve titration with cerous nitrate[36] or yttrium nitrate,[37] detecting the end point by means of methyl-red or potentiometrically.[38] Alternatively, if a known amount of calcium acetate solution is used to precipitate calcium fluoride, the excess calcium may be titrated, giving a measure of the fluoride.[39]

(c) COLORIMETRICALLY

Yellow solutions of pertitanic acid (prepared by adding hydrogen peroxide to solutions of titanium oxide in sulphuric acid) are bleached by fluoride ions owing to the formation of a colourless complex fluotitanate. This reaction may be used for the colorimetric determination of fluoride in a variety of materials.[40,41] Another widely used method utilizes the bleaching of the coloured zirconium-alizarin complex.[42] Several methods are based on the formation of the aluminium-fluorine complex using ammonium aurintricarboxylate,[43] haematoxylin[44] or Eriochromecyanin[45] to determine the change in aluminium ion concentration, and hence the amount of fluorine. Similar methods based on the iron fluoride complex make use of thiocyanate,[46] acetylacetone,[47] ferron (7-iodo-8-hydroxyquinoline-5-sulphonic acid),[48] 5-sulphosalicylic acid,[49] salicylic acid[50] and sodium bromide.[51]

(d) SPECTROSCOPICALLY

For the spectroscopic determination of fluorine, use is made of the band at 5291 A. observed when compounds containing fluorine are placed with a calcium salt on a graphite electrode and the arc or spark spectrum examined.[52] The corresponding band at 5772 A. obtained with strontium and fluorine is equally sensitive.[53] Alternatively the fluorine spectrum may be obtained by high frequency excitation of a sample containing fluoride in a sealed evacuated tube.[54]

ANALYSIS OF ANHYDROUS HYDROFLUORIC ACID.

The principal determinations made on hydrofluoric acid are of total acidity, sulphur dioxide, sulphuric acid, hydrofluosilicic acid and water. Because of its volatility, sulphur dioxide is usually determined first, by addition of iodide-iodate mixture and back-titration with thiosulphate. Total acidity is determined by titration with standard caustic soda solution to the phenolphthalein end point. Sulphuric acid is similarly determined on another portion after removing hydrofluoric acid by evaporation. Silicon compounds

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are determined by evaporating to dryness in the presence of potassium chloride and titrating the resulting potassium fluosilicate with potassium hydroxide. Alternatively the silicon may be determined colorimetrically as the yellow silicomolybdate, boric acid being used to prevent interference by fluoride. Water may be determined by means of the Fischer reagent.[55-59]

ANALYSIS OF ORGANIC COMPOUNDS

In order to determine fluorine in organic compounds, it is necessary to convert the fluorine into an ionisable form, so that the fluoride may be determined by the usual methods such as titration with thorium nitrate, or as lead chlorofluoride. Fusion with metallic sodium, or preferably metallic potassium, in an evacuated glass tube[60,61] or in a nickel bomb[62] is of general application, whilst fusion with sodium peroxide may be used for decomposing most organic fluorine compounds.[63] Alternatively the organic compound may be decomposed by dissolving it in liquid ammonia, and treating the solution with sodium.[64] Organic fluorine compounds may be decomposed by mixing with calcium carbonate and burning in a stream of oxygen in a platinum tube; the fluorine is fixed as calcium fluoride which may be weighed after removing the excess calcium compounds.[65] Other methods of decomposition include passing the vapours from the fluorocompound over heated silica, when silicon tetrafluoride is formed which may be absorbed in water or alkali; the fluorine is determined in the solution,[66, 67] or it may be absorbed on alumina in a weighed tube.[68] By combustion in a platinum tube in a stream of oxygen saturated with water vapour, the fluorine in organic compounds is converted into hydrofluoric acid which may be titrated alkalimetrically after absorption in water.[69]

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SECTION XI.

BIOLOGICAL PROPERTIES OF FLUORINE

By G. M. DYSON

TRACE ELEMENTS

Apart from the elements present in animal and vegetable systems in substantial proportions, viz., carbon, hydrogen, oxygen, nitrogen, sulphur, calcium and phosphorus, it was early recognized that small amounts of other elements - iron, magnesium, silicon, chlorine, sodium and potassium - are necessary[1-3] for the growth of the organism. Since then it has been shown that yet other elements, notably iodine, fluorine, copper, manganese, boron, molybdenum, vanadium, zinc and cobalt in trace quantities are also essential bio-elements.[4-11] It is a moot point whether tin, arsenic, selenium, silver and chromium have been proved to be essential, but there is no doubt of their presence in animal and vegetable matter,[12-14] and it is highly probable that future experiment will show that other trace elements are necessary.

During the past thirty years, attention has been focused on the part played by fluorine in animal and vegetable economy; Spiro[15] in 1926 summarized the then extant knowledge of the biological role of fluorine as a 'trace element'; by 1936[16-19] an extensive literature was already in existence, and the recognition that fluorine could accumulate in the animal system directed attention towards the occurrence of the element in foodstuffs (see page 6). A particularly useful paper[20] discusses the probable daily intake of fluorine in ordinary diet, which in adults is assessed at 0·18-0·30 mg. In infants up to four months the daily intake may rise as high as 0·46 mg., and at twelve months to 1·123 mg. owing to the presence of homogenized bone in certain 'formulæ' for infant feeding. Since the fluorine content of animal foodstuffs (milk, meat etc.) depends on that of the herbage on which the animal feeds, and thus vicariously on that of the soil on which the herbage is grown, the use of rock phosphate as a fertilizer influences the daily fluorine intake;[21] this is, however, held to have no serious biological effect.

The subject of the biological functions of fluorine may conveniently be sub-divided thus:-

1. Preservative and Bactericidal Action.
2. Effect on Vegetation.
3. Effect on Insects.
4. Effect on Enzymes.
5. Fluorine in the Human Animal System.
   - *a.* Metabolism
   - *b.* Acute Poisoning
   - *c.* Chronic Poisoning
   - *d.* Industrial Hazards
   - *e.* Dental Effects.

PRESERVATIVE AND BACTERICIDAL ACTION

Under experimental conditions, fluoride ion has been shown to exert a bacteriostatic effect on a variety of organisms. The intimate relationship of fluorine to dental caries has induced examination of the action of fluoride ion on *Lactobacillus acidophilus*, to which it is bacteriostatic at concentrations of 1:2000 - 1:4000 of sodium fluoride.[22] A bibliography of this activity is given by Bibby and v. Kesteren,[23] and others have shown[24] that there was a progressive decrease in the number of children (63·5 to 47·3% in three years) with a high mouth-count of *L.acidophilus* in an area where the fluoride content of drinking water was brought up to 1 p.p.m., whereas in an adjacent area where the water was fluorine-free the count remained the same.

Sodium fluoride has been shown to exert a pronounced cidal action towards the *Mycodermae* found in olive pickling;[25] various species of *Mucor, Torula* and *Penicillium*;[25] *Aspergillus niger* (in the growth of which the formation of citric acid was completely suppressed by 0·01 M-NaF);[26] *Microthamnion Kützingianum(Naeg.)*, which is inhibited by concentrations of 0·001% of sodium fluoride;[27] and certain yeasts.[28] In the latter case, and with *Propionibacterium pentosaceum*,[29,30] a substantial degree of tolerance can arise, and it has been suggested that this is due to the development of an alternative enzymic route in the metabolism of the organism, which is not susceptible to fluoride inhibition. In similar fashion, the fermentation of sucrose and glucose by certain *Streptococci*,[31] by *Escherichia coli*[32,33] and by *B.proteus X19* is inhibited by fluorides. Fluorides are moderately effective in inhibiting the growth of *Thiobacillus thio-oxidans*,[34] and of *Azotobacter*[35] but show little activity against the spores of *B. anthracis*[36] or the trematode *Schistosoma Mansoni*;[37] on the other hand the parasite *Trichomonas vaginalis* is killed by dilutions of 1:1000 of sodium fluoride.[38] Fluorides have no effect on psittacosis virus,[39] although they have a strong inhibitory action on the virus of foot-and-mouth disease (see page 244).

Attempts have been made to utilise the bactericidal activity of hydrofluoric acid and the fluorides; in the foodstuffs industry dilute hydrofluoric acid is an excellent antiseptic wash for barrels, process vessels and equipment for fruit juices, but its poisonous nature precludes its use except in circumstances where it can be prevented with certainty from contaminating the foodstuffs.[40] Fluorides appear to have little value as preservatives for adhesives,[41] although 0·5% of sodium fluoride has proved satisfactory as a preservative in electrolytic recorder paper.[42]

Fluorides and silicofluorides have some preservative action on timber; paint containing 5% by weight of sodium fluoride, calculated on the pigment present, protects timber against attack by *Coniophora cerebella*.[43] Conditions for the penetration of different timbers have been determined;[44] the progress of penetration can be measured by observing the effect of sodium fluoride on the colour reaction between zirconium oxyfluoride and sodium alizarinmonosulphonate; in mine timbers the protection given by sodium fluoride is less satisfactory than that by zinc chloride (7·7 years against 13·3 years; untreated control timbers having a useful life of 3·8 years).[45] The ease with which simple fluorides are leached from timber is important and is governed by the ability of the timber to fix the preservative rather than by its solubility in water. Thus, for timbers not exposed to rain, zinc chloride appears to be a better preservative than sodium fluoride; for timber exposed to weathering the reverse is true.[46] Acid potassium fluoride, and the silicofluorides of zinc and magnesium, have been found effective in protecting timber against boring insects.[47] The great difficulty in assessing wood preservatives lies in devising suitable accelerated service tests.[48] The subject has been reviewed.[49,50]

In the treatment of hides, complete disinfection was obtained[51] with sodium acid fluoride, $NaHF_2$, at 1: 10,000; and this has been confirmed by an examination of the effect of $NaHF_2$ on all the organisms (91 varieties) associated with hide and calf skin contamination.[52] Moreover, the viruses of vesicular stomatitis[53] and foot-and-mouth disease[51] are destroyed by sodium acid fluoride solution (1: 10,000). In rubber plantation practice, treatment of the tree roots with sodium fluoride solution eliminates destruction from Kok-sagyz.[54]

In yeast fermentation the use of about 1 part of sodium fluoride per 100,000 of medium not only engenders a favourable pH, reducing the usual sharp increase in acidity, but also keeps down the growth of foreign organisms.[55,56] The tendency of sodium fluoride to inhibit the degradation of reserve plant materials is utilised in preparations to prolong the life of cut flowers;[57] and it has been shown that fluorides inhibit the auxin activity in plant growth.[58]

PHYTOCHEMICAL ACTIVITY

Most vegetation is susceptible to an atmosphere containing traces of fluorine or hydrofluoric acid; this is particularly true of *Gladiolus*[59,60] in which a concentration as low as 0·05 p.p.m. produces leaf-scorch simulating *Botyritis* blight. Atmospheric fluorine contamination can arise from the combustion of coal,[61] from superphosphate plants and from aluminium reduction plants;[62-64] in one instance vegetation collected 90 miles from such a plant showed 6 - 15 p.p.m. of fluorine and within a 20 mile radius the same species showed 30 - 1400 p.p.m., with leaf-scorch roughly proportional to the HF content. The abnormally high fluorine content of Tennessee forage is found to be due to atmospheric hydrogen fluoride and not to high soil fluorine.[65] Means of dealing with such fumes are described,[66] and a sensitive and specific reagent for detecting hydrofluoric acid in air is a strip of paper dipped in hæmatin solution.[67] The fluorine compounds absorbed by trees from the atmosphere are retained in the bark;[68] new shoots are fluorine free if the surrounding atmosphere is fluorine free and the fluorine content of such shoots is a valuable indication of contemporary contamination. Fluorine-smoke contamination of leaves may be detected by washing them with water in which the contaminant fluorine compounds dissolve leaving the normal fluorine content of the leaves untouched;[69] the presence of fluoride in washings may be detected by inhibition of the acid phosphatases of shoot cuticle[70] or by the isolation of sodium silicofluoride, Na_2SiF_6.[71,72] The use of sodium fluoride as a defoliant, causing total leafdrop,[73] and as a herbicide has been reported.[74]

The toxicity to plants of silicofluorides appears to be greater than that of fluorides;[75] for example, severe damage to greenhouse plants has arisen from the use of silicofluorides as wood preservatives.[76,77] Despite claims[78] that minute traces of hydrofluoric acid exert a beneficial effect on barley germination, or are at least without positive action,[79] the consensus of opinion - as exemplified by the extensive work of Morse[80] - is that the presence of soluble fluorides in soil up to 100 p.p.m. greatly diminishes, and that 400 p.p.m. completely inhibits, the germination of maize. The effect of insoluble fluorides such as that of calcium is less pronounced.[81-88]

The widespread agricultural use of superphosphate made from phosphate rock rich in fluorine, some of which is retained by the finished product, has been studied in detail. There is no doubt that ground phosphate rock itself may contain sufficient available fluorine to be inimical to plants;[89] on the other hand manufactured superphosphate has lost so much of its fluorine as to have no appreciable toxic effect on vegetation.[90-94]

EFFECT ON INSECTS

Fluorides and silicofluorides are excellent insecticides and well-documented reviews of this topic are available.[95-102] The toxicity of elementary fluorine itself to insects generally is approximately equal to that of hydrogen cyanide.[103] The fluorides and silicofluorides are comparable in insecticidal activity and their action against various organisms is shown in Table I.

TABLE I. - INSECTICIDAL ACTIVITIES OF FLUORIDES AND SILICOFLUORIDES

Organism	Substances used	Reference	Activity
Pyrausta nubilatis (European cornborer)	$BaSiF_6$, $CaSiF_6$, Na_2SiF_6	105	All active; $CaSiF_6$ showed highest activity with least plant injury.
Bombyx mori (Silkworm)	Na_3AlF_6, K_2SiF_6, K_3AlF_6, $BaSiF_6$, Na_2SiF_6, $(NH_4)_2AlF_6$, NaF, MnF_2, PbF_2, MgF_2	106	Substances arranged in order of increasing toxicity.
Calliptamus Italicus *Hypera(Phytonomus) variabilis* *Rhynchitis auratus ferganensis* *Agrotis segetum* *Lymantria dispar*	$BaSiF_6$, NaF, Na_2SiF_6	107	Except against *C.Italicus*, all are superior to calcium arsenate and lead arsenate.
Anthonomus eugenii (Cano) (Pepper weevil)	Na_3AlF_6, K_3AlF_6, $BaSiF_6$	108	Killed more easily than calcium arsenate, but considerable plant injury.
Cydia pomonella (Codling Moth)	$BaSiF_6$, K_2SiF_6, cryolite	109,110	Toxicities lower than calcium arsenate on a w/w basis.
Merulius lacrymans (Dry rot)	$ZnSiF_6$	111	Excellent activity.
Epitrix parvula (Tobacco leaf beetle) *Epitrix cucumeris* (Potato flea beetle) *Epitrix fuscula* (Eggplant flea beetle) *Epilachium corrupta* (Mexican bean beetle) *Trilobium confusum* (Flour beetle)	Na_3AlF_6 (Natural cryolite)	112	Specific poisons 2 to 2·5 times as effective as magnesium arsenate.
Ctènocephalides canis *Ctenocephalides felis*	NaF(10%) + inert dust	114	All showed similar high toxicity.
Forficula auricularia (Earwig)	NaF	115	Satisfactory control.
Eomenacanthus stramineus (Poultry lice)	NaF	116,124	Satisfactory control.
Meniophon gallinae *Gomocotes hologaster* (Moths)	NaF	117	Useful mothproofing agent.
Blatella germanica (Cockroach) *Periplaneta americana* (American roach)	NaF, Na_2SiF_6	118,119 122,123 131^{1},132 135,136	Good controlling agent as stomach, as well as contact, poison.
Formica exsectoides (Ants)	NaF	120,125	Good control.
Gryllotalpa vulgaris (Mole cricket)	NaF, cryolite, Na_2SiF_6	121	75 – 80% kill.
Culex pipiens (Mosquito larvæ)	NaF	122	Gives an account of histopathological changes.
Bovicola bovis (Cattle lice)	NaF	126	Controls adequately.
Termes nemorosus (Termites)	NaF, Na_2SiF_6	128 130,134	Controls adequately.

TABLE I (continued)

Organism	Substances used	Reference	Activity
Desmoris fulvus *D. constrictus* (Sunflower seed weevils)	NaF	129	Controls adequately
Liponyssus silviarum (Fowl mite)	NaF	137	Comparable with nicotine sulphate.
Byturus bakeri (Raspberry worm)	NaF	133	Successful, but leaves toxic residues.
Callosobruchus maculatus (Cowpea weevil)	HF	139	HF from 2 oz. CaF per 1000 cu.ft. completely destroys.
Thermobia domestica (Firebrat)	NaF, Na_2SiF_6, $BaSiF_6$, Na_3AlF_6	138	Arranged in order of increasing toxicity.
General	NaF, Na_2SiF_6, $MgSiF_6$, $CaSiF_6$, $BaSiF_6$, $Al(SiF_6)_3$, MnF_2	113, 127	All showed similar toxicity.

[1] Describes the injection technique of assay.

There is a considerable literature dealing with the persistence of fluorine compounds on fruit sprayed therewith against insect infestation. When fluorides or silicofluorides are dusted over apples, pears or similar hard fruits it appears that, even after some months have elapsed and the fruit is ripe, a considerable amount of fluorine-containing compounds remains on the surface. In view of the high toxicity of fluorine compounds, this has been the subject of much investigation. With fruits such as apples, much of the fluorine can be removed by washing with dilute hydrochloric acid, and this has become standard practice. Subsequent rinsing with water and drying are of course necessary. In the United States of America the official tolerance is 0·01 grain of fluorine per lb. of fruit and it has proved difficult in many cases to reduce the fluorine content of softer fruits to this limit. For example, whilst the washing of apples and pears with dilute hydrochloric acid is feasible, the similar washing of grapes, apricots or peaches is not. The use of silicofluoride dustings on grapes has led to fears that excessive amounts of fluorine would be found in the wine produced from them. This, apparently, is not true; during the process of vinification the fluoride is precipitated and the wine when ready for bottling contains no more fluorine than do control preparations from grapes not treated with fluoride-containing materials.[140] The consensus of opinion is that sprays involving powdered cryolite generally produce less toxic residues than those made from the fluorides or silicofluorides.[141-144] Several useful general reviews on the subject have been published[145-148] and literature relating to specific crops is available on apples,[149-162] oranges,[163] squash[164] and cabbage.[165] Detailed methods have been worked out for the analytical determination of fluorine in insecticides of this type.[166]

EFFECT ON ENZYMES

There is a very considerable volume of literature dealing with the inhibitory effects of fluorides or of fluoride ion on enzymes. It is beyond the scope of this volume to go into this matter in detail but some of the salient papers and their results are summarized in Table II.

TABLE II. - EFFECT OF FLUORIDES ON ENZYME SYSTEMS

Organism	Inhibiting agents	Enzyme system	Effect	Reference
Animal cells	NaF	Cytochrome oxidase system	++	180
Animal tissue	NaF	Acetylphosphatase	M/100-0 M/50 +	129
Avena & *Pisum*	NaF	Coleoptile growth	++	167
Basidiomycetes	NaF	Acid phosphomonoesterase	+++	181
Blood	NaF	Clotting enzymes	++	238
Blood	NaF	Phosphatase	++	224,232
Codling moth	NaF	Respiratory enzymes	++	177
Dog	NaF	Intestinal phosphatase	+++	175
Dog liver	NaF	Serum phosphatase	0	183
Escherichia Coli	NaF	Respiratory oxidation	+++	166
Guinea-pig	NaF	Intestinal phosphatase	+++	176
Human	NaF	Salivary amylase	0	192
Human liver (damaged)	NaF	Serum phosphatase	0	178
Human lung	NaF	Amylase	++	218
Kidney	NaF	Phosphorylase	++	196,198,201,231
Kidney Liver tissue Spleen	NaF	Deamination and dephosphorylation enzymes	++	174
Milk	NaF	Peptic activity	+++	219,222,235
Muscle	NaF	Dephosphorylase	++	200,227,236
Nicotiana virus	NaF	Enzymic accumulation	0	215
Rabbit	organic fluorine compounds	Acid phosphatase (blood)	0	169
Rat-kidney	NaF	Transamination enzymes	++	209
Rat-liver	NaF	Arginase	++	212
Rat-liver	NaF	Ornithine citrulline system	--	172
Ricinus	NaF	Lipase	++	217,233
Rickettsiae	NaF	Enzymic acceleration	0	215
Sheep brain	NaF	Acid phosphatase	++	168
Soya bean	F ion	Phosphatase	+++	221
Soya bean	NaF	Urease	+++	234,239
Yeast	NaF	Adaptive fermentation of galactose	++	210,211
Yeast	NaF	Cell permeability	+	170,171
Yeast	organic fluorine compounds	Fermentation	0	169
Yeast	NaF	Fermentation by	++	184,186,228,237
Yeast	NaF	Glycogen storage	++	225
Yeast	NaF	Multiplication	-	182
Yeast	NaF	Respiration	++	185,189,190,194 206,213,220
Yeast (top)	NaF	Respiration	-	187,223
"	KF	Acetylcholinesterase	?	197
"	NaF	Apozymase + cozymase	+	199,205
"	NaF	Cytochrome oxidase	0	193
"	NaF	Glucosulphatase	++	226
"	NaF	Invertase	0	208
"	NaF	Phosphatase (*in vitro*)	+	188,195,229
"	NaF	Phosphatase (*in vitro*) (reactivation of)	+++	173
"	NaF	Succinodehydrogenase	+++	203
"	F ion	Takadiastase on glycerophosphates	++	204,207,240
"	NaF	Takasulphatase	+++	202

Note:- The symbols indicating 'Effect' have the usual meanings: 0 = no effect; + to +++ = varying degrees of inhibition; - or -- = promotion.

FLUORINE IN THE HUMAN ANIMAL SYSTEM

1. Metabolism.

Since, as is shown above, fluorides have a pronounced effect on enzyme systems, mainly inhibitory, it is only to be expected that they would have a considerable effect on the course of animal metabolism. Apart from the fact that the fluorides are acute poisons in large doses, it has been shown that small doses of soluble fluorides have a profound effect on physiological metabolism. The necessity for fluorine in the animal diet is shown by nutrition experiments in which rats kept on a diet completely free from fluorine die in 48 days but can, when failing, be revived by adding small traces of fluoride to the diet.[241] The effect of fluorine on the basal metabolic rate has been determined[242] and the general effect of fluorides on carbohydrate metabolism has been extensively studied,[243-246] including the effect in relation to the carbohydrate metabolism of yeast.[247] The influence of fluorine on organic esterases has been examined,[248] as also has its influence on respiration.[249-255] The effect of fluorides on the growth of the echinoderm egg,[256] and on growth generally[257-264] shows in nearly every case that the main function of the element is to depress the rate of growth and in many cases to stop it completely. The effect of fluorine on reproduction[265-272] shows in general a tendency to induce abortion, and in most cases there is a demonstrable transfer of fluorine from the mother to the fœtus. The effect of fluoride on nerve and brain function is due to its action as a catalyst inhibitor;[273-277] the excretion of fluorine has been studied,[278] and the deposition of fluorine in skin tissue and hair, where a condition of fluorine alopecia is recognized, has also been examined.[279]

There appears to be a relation[280] between the presence of fluorine in drinking water and the incidence of deafness in children; of 109,869 children examined 4·9% were found to be deaf in communities having no fluorine in their water supply, whereas only 2·8% suffered this disability in communities where the water contained traces of fluorine. The use of radioactive fluorine for the study of fluorine metabolism has been studied by Wills[281] and his results, in general, confirm those obtained by more orthodox experimental methods.[282-284] The general problem of fluorine in nutrition will be considered later (see page 251). Sodium fluoride has been used as an anti-coagulant for blood,[285-288] in which connexion it appears to have about 1/20th of the activity of heparin. The influence of fluorides on blood pressure has also been carefully studied;[289-298] the effect of fluorides on heart function is very largely bound up with action on the dehydrogenase systems.[299,303] Another manifestation of the influence of fluorides on animal enzyme systems appears to be the inducing of hyperglycæmia on the injection of sub-lethal doses of fluorides; this may be counteracted with insulin.[304-306] On the other hand the effect of prolonged ingestion of small quantities of fluoride on the thyroid system is obscure.[307-313]

The influence of fluorides on cell metabolism is quite marked. Although the fluoride ion has little, if any, action on the oxygen consumption of the cells it markedly reduces anaerobic glucolysis. This is particularly shown with cancer cells.[314-328] Fluorine compounds, however, have not been shown to have any active influence on the growth of tumours.[329-331] The large number of instances given above in which fluoride ion is shown to have some activity in animal metabolism arising from an interference with the enzyme systems has been turned to account in experimental therapeutics by using fluorides to counterbalance excessive activity of enzyme systems; one particular application which has been successfully pursued over a number of years is in the treatment of hyperthyroidism,[332-337] and exophthalmic goitre.[338,339] Attempts have also been made to use the antiseptic effect of fluoride solutions in the treatment of oral infections and wounds.[340,341]

Refs. p. 251

2. *Acute Poisoning.*

The terminology of this subject is somewhat obscure; the term 'fluorine poisoning' is commonly used where the active agent is a fluoride or a silicofluoride. It is clear that this term should be restricted to the poisoning observed with the element itself and that the poisoning observed with HF, fluorides or silicofluorides should be referred to as such. The literature on true fluorine poisoning is scanty; very little experimental work has been done on the activity of the element itself. An important contribution[344] by Stokinger *et al.* indicates that three hours' exposure to an atmosphere containing 200 p.p.m. of fluorine by volume is fatal to experimental animals and that an atmosphere with 100 p.p.m. gave an overall mortality of 60% within a fortnight. The tolerated concentration of fluorine in the atmosphere appears to be about 7 parts per million and this is very much higher than the corresponding figure for hydrofluoric acid (1 p.p.m.). Murray and Wilson[343] have given a documented survey of the potential hazards from elementary fluorine in this country, and the statement has been made by Machle and Evans[342] that five years of intermittent exposure to concentrations of elementary fluorine, such as are harmful to experimental animals, was tolerated by a group of industrial workers without clinical evidence of damage and without injury to the blood visible on hæmatological examination.

The hazards associated with hydrofluoric acid lie largely in its corrosive action in contact with the skin, which is dealt with below; there appears to be no record of the use of hydrofluoric acid in criminal poisoning. The subject of acute fluoride poisoning by soluble fluorides has been reviewed.[345] Although it has been said[346] that an oral dose of 320 mg. per day of sodium fluoride over a period of five to six months is without toxic effect on man, there are nevertheless numerous instances[347-350] of accidental poisoning with sodium fluoride or sodium silicofluoride. In one case a man took half a teaspoonful of insect powder in mistake for a medicine and died 10 hours later. The material was essentially sodium silicofluoride and the dose could not have exceeded 2 grams. There are also examples of mass poisoning; in 1943, 263 persons were accidentally poisoned with sodium fluoride, of whom 47 died; in another instance in the same year 71 non-fatal cases of acute fluoride poisoning were observed following the deliberate addition of sodium fluoride to a chocolate pudding.[350,351] The latter case is an example of criminal fluoride poisoning, and another similar instance has been recorded.[352] Even among scientists, it does not appear to be generally recognized that sodium fluoride is an extremely toxic substance; this is reflected in the number of accidental poisonings which have occurred, and it has been observed, for example, that during 1941 there were 56 cases of sodium fluoride poisoning in foodstuffs in the United States as against 22 cases of accidental arsenic poisoning by the same route.[353] The antidote for sodium fluoride poisoning is the prompt administrstion of sodium nitrite[354-357] which together with hæmoglobin forms a non-toxic complex with the fluoride ion.

Sedlmeyer has reviewed the subject of fluorine poisoning generally[358] and the acute toxicity of fluorine has been examined in fish,[359] goats,[360] guinea pigs[361] and frogs.[362]

3. *Chronic Poisoning.*

The subject of chronic fluorine poisoning, particularly from mineral sources, has been reviewed by McClure[362] and by Roholm.[363] The general literature of chronic fluorine poisoning is so very extensive, amounting in all to some 500 contributions, that it cannot be fully reviewed here: a number of publications have however been noted[364-380] as giving a survey of the more strictly chemical aspects of the subject. Endemic fluorine poisoning[381-386] is common in various parts of India and in certain districts in the Argentine.

4. *Industrial Hazards.*

The chief biological hazards to be encountered in the handling of fluorine and its derivatives are:-

(*a*) The danger of poisoning arising from accidental escapes of fluorine or of hydrogen fluoride.

(*b*) The extremely corrosive action of hydrogen fluoride either in its anhydrous form or in its concentrated aqueous solutions.

(*c*) The danger of inhaling over long periods fumes containing small quantities of free or combined fluorine.

The toxicity of fluorine and hydrogen fluoride has already been discussed. Several detailed accounts have been given of the sequelæ to hydrofluoric acid burns; in general they resemble third degree burns by fire, but in addition there is the specific toxic action of the fluoride ion and healing is usually extremely slow. In many cases the necrosis can reach the bone after which the healing may take several months.[387-390] The correct first-aid treatment appears to be washing rapidly with much slightly warm water and subsequent covering of the affected parts with a paste of magnesium oxide and glycerol.[391-394] Where severe burns over a large surface are experienced the injection of calcium gluconate or calcium levulinate is recommended to counteract the toxic action of the fluoride ion. Several publications dealing with the prevention of accidents with concentrated hydrofluoric acid have appeared;[395-398] the essential features of such recommendations are, of course, those of 'good housekeeping' in the factory or laboratory, the provision of properly ventilated plant, the constant use of safety measures and protective clothing, and an intelligent appreciation of the dangers of the material.

Chronic fluoride toxicosis may arise in a variety of ways. In certain cases the production of long-lasting industrial fogs ('smog') is the cause of serious, sometimes fatal, respiratory conditions. Analysis of such fogs frequently shows the presence of hydrogen fluoride in the droplets in significant quantities.[399-404] Experiments on the absorption of irritant gases by rabbits showed that when an atmosphere containing 0·16 – 1·5 mg./l. of hydrogen fluoride was inhaled for 1·5 – 3·5 hours, all the hydrogen fluoride was absorbed by the upper respiratory tract, which was therefore acting as a concentrating or localizing mechanism;[405]—it has been shown that in the Maastal,[406] Luttich[407,408] and Meuse Valley fog catastrophies[409,410] there was, in addition to sulphur dioxide, a fairly high proportion of hydrogen fluoride in the droplets.

The hydrogen fluoride in these fogs frequently arises from effluent gases from factories; of these the chief are superphosphate factories and magnesium and aluminium refining and production plants. The production of certain types of superphosphate from sulphuric acid and phosphate rock inevitably leads to the evolution of small quantities of hydrogen fluoride from the fluoride present in the rock; this under normal circumstances is vented to the upper atmosphere and dispersed by the wind, but when atmospheric conditions are suitable and fog is formed it is possible for hydrogen fluoride to be concentrated in the fog droplets and so to cause chronic toxicity. The examination of superphosphate works in this connexion has been reported[411-413] and numerous examples are cited where both plants and animals growing in the neighbourhood of superphosphate factories have been shown to have a very abnormally high fluorine content. Bees are particularly susceptible to factory waste gases containing hydrogen fluoride and several occasions are on record where mass killing of bees by these gases has occurred.[414] Similar toxic properties have been observed with the fumes from aluminium and magnesium reduction plants; in this case, however, the control of fumes is not so easy as in superphosphate manufacture where the materials are confined to a closed system. It has been shown[415] that the concentration of fluorine in the air of rooms where aluminium cells are operated may reach 8 - 10 mg. F per 10 cu.m. In a number of cases the examination of workmen from these rooms has shown abnormally high fluorine in the bones, teeth and excreta.[416-419] Similar results have been observed in the manufacture of magnesium[420,421] and in the production of steel where sodium fluoride is used as a flux.[422] In industries where cryolite is mined or ground, or where ground cryolite is used for large scale operations, a considerable amount of occupational fluorosis has been observed.[423-428] It has been stated by Machle and Kitzmiller that the lower limit of toxic concentrations of hydrogen fluoride in air lies between 0·03 and 0·2025 mg. per litre. The lungs and liver are the organs most severely and constantly affected,[429] but it has been shown that concentrations very much lower than this are inimical, as the fluorine is very largely stored in the body. The mechanism appears to be first, concentration in the upper respiratory tract, and then absorption into the rest of the systen with storing in bones and teeth as the final resting place.

5. Dental.

There have been some thousands of papers contributed to the chemical and medical press concerning the relation of fluorine in various forms and the hygiene of the teeth. It would not be appropriate to review the whole of this literature here but a selected list of references is given[430-490] in which attention is drawn to summaries and well-documented reviews of the subject. In general it appears established that the entire absence of fluorine from the diet leads to the faulty formation of dentine in the teeth of growing mammals. On the other hand more than a certain limiting quantity (the consensus of opinion being that this should be approximately 1 part per million of the general intake of food and drink) leads to a condition of the teeth known as 'mottling', and if this limit is seriously exceeded, to malformation of the teeth. In other words it appears to be established that the intake of fluorine should be controlled between very close limits. There is, naturally, some latitude of opinion as to the extent of these limits. From this observation has arisen the difficult problem of public hygiene as to whether it is expedient to add fluoride ion to public water supplies. It is clear that if the sole source of fluorine in the animal system were the drinking water, it would be safe to add fluorine in such a way that the concentration in this water approached 1 p.p.m. or possibly slightly exceeded this figure; on the other hand various foodstuffs (see page 6) have been shown to contain varying quantities of fluorine, often largely in excess of the 1 p.p.m. recommended. It is therefore uncertain whether the addition of fluorine to the general supply of drinking water will raise the total intake of fluorine above the desired limit and into an undesirably high range, and this has been a much argued problem in public hygiene (see also page 7).

In view of the very considerable importance of the estimation of small quantities of fluoride ion in biological materials[491-494] special methods have been worked out for the routine examination of organs and animal tissues,[495,496] blood,[497] meat,[498] wheat and flour[499] and gelatine,[500] and a series of papers has been published on the histology of organs and teeth which contain fluorine in excess of normal amounts.[501-505]

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CHAPTER 2

CHLORINE

SECTION XII

THE OCCURRENCE, PREPARATION AND MANUFACTURE OF CHLORINE.

By W. W. SMITH

THE OCCURRENCE OF CHLORINE.

IN STARS AND NEBULÆ

OVER the last few years, attention has been given to the determination of the spectra and chemical composition of nebulae and stars, and some information on the presence of chlorine in these bodies is available. Thus measurements have been made of the emission lines of the gaseous nebulæ NGC 6572, 7027, 7662[1] and, from these, permitted and forbidden transitions of chlorine in the neutral and ionized state have been identified. The abundances of chlorine and oxygen, relative to hydrogen = 1000, have been estimated as 0·002 and 0·25 respectively in planetary nebulæ, a result claimed to be similar to that found for the sun and for the nebulæ NGC 6572, 7027 and 7662.[2] Evidence for the presence of chlorine in stellar atmospheres has been obtained by measurements of the spectra of U Cygni,[3] γ Pegasi[4,5] and U Sagittarii.[6] The observations for γ Pegasi[4] indicate that the abundance ratio for chlorine/oxygen is in accord with that given above for nebulæ.

TERRESTRIAL CHLORINE

The hypothesis has been advanced that chlorine existed in the primordial atmosphere of the earth and that subsequently it entered the hydrosphere[7]. Chlorine is now widely distributed throughout the whole of Nature and is found in minerals, the oceans, river water, the atmosphere, and in plants and animals.

However, except in the gases from volcanoes (see below), it is not found in the free state. Among the elements it is reckoned 15th in order of abundance in igneous rocks,[8] whilst older calculations[9] place it as 11th if the average composition of all terrestrial matter, including rocks, the sea and the atmosphere, is taken into account.

IN ROCKS AND MINERALS

The average chlorine content of volcanic rocks is quoted as 0·048%[7] while figures for 28 classes of eruptive rocks have also been determined.[10] The most recent work[11] on igneous rocks, which constitute about 95% of the crust of the earth,[12] gives an average figure of 0·0314%, determined on 23 rocks in the U.S.S.R.; this figure is considerably lower than the 0·097% given in the earlier compilation of Clarke.[9] Analyses recently carried out on 16 metamorphosed sedimentary rocks in the Aulanko area in south-western Finland gave an average chlorine content of 0·035%.[13] The chlorine content of soils and peats is of the same order as that of igneous rocks.[11,14] The skeleton of the coral contains 0·038% of chlorine.[15]

Since vegetation contains chlorine (see below), it is not surprising that coal formed from it also contains the element. Since, however, the coal in its formation has been subjected to high temperatures, some of the chlorine present only as chloride ion in the vegetation might be expected to be converted into chloro-organic compounds. This appears to be so: in determinations on 22 coals from many countries, the total chlorine varied from 0·03 to 0·33%; the amount of chlorine probably combined organically ranged from 0 to 0·12%.[16] In tests on the water-soluble chlorine content of coal from various areas in northern England, figures of 0·002% to 0·355% were obtained.[17] Tests on 24 coals from 12 states in the U.S.A. gave chlorine contents of 0 – 0·46%, with a mean value of 0·128%; the authors point out that the extraction of the powdered coal with water may give slightly low results for chlorine, again indicating the possibility of chloro-organic bodies.[18]

Chlorine is found in the following minerals which are supplementary to those mentioned in the original treatise (Mellor, II, 15) :-

Normal Halides:[19, 20]
Chloromagnesite, $MgCl_2$
Hydrophilite, $CaCl_2$
Eriochalcite, $CuCl_2,2H_2O$
Chloraluminite, $AlCl_3,6H_2O$
Ostwaldite, colloidal AgCl.

Oxyhalides and Hydroxyhalides:[19, 20]
Lorettoite, $Pb_7O_6Cl_2$(?)
Daviesite, a Pb oxychloride – formula not known
Bismoclite, BiOCl
Kempite, $Mn_2(OH)_3Cl$
Bolallackite, $Cu_2(OH)_3Cl,H_2O$(?)
Cadwaladerite, $Al(OH)_2Cl,4H_2O$
Diaboleite, $Pb_2CuCl_2(OH)_4$
Chloroxiphite, $Pb_3CuO_2(OH)_2Cl_2$(?)
Koenenite, $Mg_5Al_2(OH)_{12}Cl_4$
Kleinite, $Hg^{\cdot\cdot}(NH_4)$ chloride - sulphate
Mosesite, $Hg^{\cdot}(NH_4)$ chloride - sulphate
Petterdite, a Pb oxychloride
Sarawakite, probably an Sb oxychloride.

Halide complexes:[19, 20]
Pseudocotunnite, K_2PbCl_4
Mitscherlichite, $K_2CuCl_4,2H_2O$
Chlormanganokalite, K_4MnCl_6
Huantajayite, (Na,Ag)Cl
Baumlerite, $CaCl_2,2KCl$
Kremersite, $FeCl_3,2NH_4Cl,H_2O$
Schwarzembergite, $Pb(IO_3)_2,3PbO_2Cl_2$.

Compound halides:[19]
Trudellite, $Al_{10}Cl_{12}(OH)_{12}(SO_4)_3,30H_2O$(?)

Carbonates containing Halogens:[19, 20]
Northupite, $Na_3MgCl(CO_3)_2$

Borates containing Halogens:[19]
Teepleite, $Na_2B_2O_4,2NaCl,4H_2O$
Bandylite, $CuB_2O_4,CuCl_2,4H_2O$
Hilgardite and Parahilgardite, $Ca_8(B_6O_{11})_3Cl_4,4H_2O$.

Sulphates containing Halogens:[19, 20]
Caracolite, a basic NaPb chloride - sulphate – formula not known
Chlorothionite, $K_2Cu(SO_4)Cl_2$
Schairerite, $Na_3(SO_4)(F,Cl)$

Sulphates containing Halogens:[19,20] (continued.)
Sulphohalite, $Na_6ClF(SO_4)_2$
Connellite, $Cu_{19}(SO_4)Cl_4(OH)_{32},3H_2O$ (?)
Buttgenbachite, $Cu_{19}(NO_3)_2Cl_4(OH)_{32},3H_2O$ (?)
Spangolite, $Cu_6Al(SO_4)(OH)_{12}Cl,3H_2O$
Kainite, $KMg(SO_4)Cl,3H_2O$.

Compound sulphates:[19]
Hanksite, $Na_{22}K(SO_4)_9(CO_3)_2Cl$
Wherryite, $Pb_4Cu(CO_3)(SO_4)_2(OH,Cl)_2O$ (?)

Phosphates, Vanadates and Arsenates containing Halogens:[19,20]
Chlorapatite, $Ca_5(PO_4)_3Cl$
Svabite, $(Ca,Pb)_5(AsO_4,PO_4)_3(F,Cl,OH)$
Hedyphane, $(Ca,Pb)_5(AsO_4)_3Cl$
Ellestadite, $Ca_5(Si,S,P,CO_4)_3(Cl,F,OH)$
Sampleite, $NaCaCu_5(PO_4)_4Cl,5H_2O$
Kampylite, $Pb_5[(As,P)O_4]_3Cl$
Polyspharite, $(Pb,Ca)_5(PO_4)_3Cl$
Georgiadesite, $Pb(AsO_4)_2,4PbCl$.

Arsenites and Antimonites containing Halogens:[19,20]
Ecdermite and Heliophyllite $Pb_6As_2O_7Cl_4$(?)
Finnemanite, $Pb_5(AsO_3)_3Cl$
Nadorite, $PbSbO_2Cl$
Ochrolith, $[PbCl]_4(SbO_3)_2[Pb_2O]$.

Silicates containing Halogens:[20]
Nasonite, $Ca_4Pb_4(Si_2O_7)_3,(PbCl)_2$
Hackmanite, $Al_2Na_4(SiO_4)_3.[Al(Cl,SNa)]$
Lasurite, $Al_2(Na_2Ca)_2(SiO_4)_3,Al(NaSO_4,S_3Na,Cl)$
Marialith, $3NaAlSi_3O_8,NaCl$
Friedelite, $H_{16}Mn_{11}(SiO_4)_{10}(MnCl)_2$
Pyrosmalith, $H_{16}(Fe,Mn)_{11}(SiO_4)_{10}[(Fe,Mn)Cl]_2$.

Organic Compounds:[19]
Calclacite, $CaCl(C_2H_3O_2),5H_2O$.

IN METEORITES

The mean chlorine content of siliceous meteorites is quoted[7] as 0·08% and 0·09%. Iron meteorites often contain considerable amounts of ferrous chloride; *e.g.*, 0·363% of chlorine was found in a specimen of octahedrite from Glasgow, Barren County, Kentucky.[21]

IN VOLCANIC GASES

A trace of free chlorine has been found in the gases of Kilauea, Hawaii.[22] In other cases it was found that, at 1200°C. and at 760 mm. pressure, the volume per cent of free chlorine was 1·03 – 1·33.[23]

Hydrochloric acid and chlorides are also found in the products of volcanic activity. Thus the fumarolic incrustations in the Valley of Ten Thousand Smokes were found to contain 0·05% of sodium chloride.[24] In the Katmai region of Alaska, fumarole vapours contained hydrochloric acid as well as iron, zinc, and ammonium chlorides.[25] The quantity of hydrochloric acid contained in these vapours can be very large. Thus it has been estimated that, in 1919, at 100°C. and 760 mm., the volume of steam emitted by the fumaroles in the Valley of Ten Thousand Smokes was $2{\cdot}6 \times 10^4$ cu.m. per sec.; the steam contained 0·117% of hydrochloric acid, equivalent to a yearly emission of $1{\cdot}3 \times 10^6$ metric tons of acid.[26] The role of such chlorine-rich gaseous or liquid emanations in the formation of such materials as the chlorine-containing silicates known as scapolites has been discussed.[27]

IN THE ATMOSPHERE

Very little information is available on the direct determination of chlorine in the atmosphere, but many analyses have been carried out on rain, snow, fog and frost.

In the neighbourhood of Chionji, Kyoto, Japan, the average Cl content of the air was 7·3 μg. per cubic metre.[28]

IN RAIN AND SNOW

Chlorine is found as chloride in the various forms of precipitation. Although, as shown in the work reviewed, the chloride is believed to arise mainly from salt spray carried in from the oceans, the figures quoted are for chloride ion and not for sodium chloride.

During the period 9th October 1919 – 22nd May 1920, 48·13 lb. of chloride fell per acre in Mount Vernon, Iowa, U.S.A.[29] Over the period 1st October 1922 – 1st June 1923, the quantity of chloride was 20·35 lb. at the same place;[30,31] in samples of 12 snows and 29 rains the chloride content varied from 3·54 to 28·1 p.p.m.[31] The chloride was considered to originate as salt spray carried from the Atlantic coast. Measurements made in the same area over the period 14th June 1936 – 5th June 1937 gave chloride contents in rain and snow ranging from 0·7 p.p.m. on 27th May 1937 to 11·15 p.p.m. on 19th February 1937.[32] The lowest figures occurred at a time of heavy rainfall while the highest were either preceded by several weeks of drought or were associated with dust storms.

Results are also available for similar work carried out at Cornell College, Iowa, U.S.A. where, over the period 19th September 1921 – 2nd June 1922, the rain and snow which fell, equivalent to 17·46 inches of rain, carried with them 7·942 lb. of chloride per acre, equivalent to an average concentration of 2·01 p.p.m. in the precipitation.[33] Determinations made at a station 6½ miles from the Cumberland coast in England showed that, during a period of strong wind from the sea, the chloride content of the rain was as high as 137 p.p.m.; in calm weather, a figure of 7 p.p.m. was recorded. The figures were higher during winter, averaging 22 p.p.m. in October – December 1920; at Maryport on the coast these three months gave an average of 121 p.p.m.[34]

A review of published analyses of rain water given by Riffenburg in 1925 indicated an average of about 3 p.p.m. of chloride for the figures reported in over 200 journal articles; continuation of the survey of the literature was held to support this figure. The amount of chloride was shown to depend on location, particularly on proximity to the open sea, values as low as 0·05 p.p.m. being obtained in inland districts, and as high as 45 p.p.m. in Hawaii.[35] Analyses of rain water at different places in Mauritius showed that over the period 1934 – 1936 the average annual chloride content varied between 14·36 and 29·43 p.p.m. The chloride content increased with rainfall.[36]

Measurements in Sweden of the chloride content of mountain fog frost gave an average of 3·6 p.p.m., and of snow, 2·1 p.p.m., but the figures were very variable depending on the manner of formation of the crystals, well-formed crystals being almost free from chloride.[37] Figures for fog and cloud have also been obtained,[38] 7·5 p.p.m. for fog at Kent Island, Nova Scotia, 35 p.p.m. on the S.E. coast of Massachusetts and 0·1 p.p.m. for cloud on Mount Washington, New Hampshire, U.S.A.

Recently, the results of Israël[39] and of others have been reviewed.[40] In all, 252 observations in industrial, agricultural and mountain districts in

Western Europe were considered. The chloride content of rain was found to show the remarkable variation of 0·08 – 171·0 p.p.m. at Leiden, while smaller ranges were experienced at Haid and at Donnersberg; for snow, the figures varied between 0·35 p.p.m., recorded on the Sonnblick Massiv, to 30·97 p.p.m. at Donnersberg.

The reports considered above show wide variation in results, and in view of this and of the absence of comprehensive data for Asia and the other land masses, it is clearly impossible to compute an average figure for the chlorine content of rain or snow. Amounts of chloride appear to be dependent mainly on proximity to the sea and the incidence of on-shore winds. Hence, like the rainfall figure itself, the chloride content of precipitation would have to be determined for each particular locality in question.

IN THE SEA

There is a large literature on this subject[41] and for this Supplement it will suffice to indicate the range of values obtained. It has been calculated[7, 42] that there are 278 kg. of sea water for every square centimetre of the earth's surface, and only 4·5 kg. of continental ice, 0·1 kg. of fresh water and 0·003 kg. of water vapour. When it is borne in mind that the sea contains approximately 1·9% of Cl and that only a few inland waters such as the Dead Sea in Palestine and Searles Lake in California contain Cl in higher concentration than this, the overwhelming importance of the sea in comparison with the other aqueous sources of chlorine becomes evident.

Chloride ion is the major constituent of sea water, being present to the extent of 18·97 g./kg. while the bromine concentration is 0·065 g./kg. and the total solid content 34·33 g./kg., giving ratios of Cl/Br = 292, and of total solids/Cl = 1·81.[43] Earlier figures for the Strait of Georgia, British Columbia, gave a Cl/Br ratio of 279[44] as compared with the value of 288 obtained by Winkler[45] for the Adriatic. For water near the north-east coast of the Black Sea, the total solids/Cl ratio was 1·7911 – 1·8307; the higher values were obtained near the coast, and were higher than the normal values for ocean water.[46] In a recent study of the Cl/Br ratio of various waters[47] it has been pointed out that the value is but slightly influenced even locally, e.g. in the Sea of Azov or the Baltic Sea, by influx of river water. The many underground waters having Cl/Br ratios of about 300 are probably normal sea water held in sediments which were deposited on submerged coastal plains. Waters having Cl/Br ratios of less than this value rarely occur, and are usually associated with tropical and subtropical coastal salt lakes which have become more or less isolated. The lower ratios arise from deposition of sodium chloride as a result of evaporation. Higher Cl/Br ratios than 300 are probably caused by the leaching of salt deposits rich in chlorides. The distribution of chlorine between sea water and sediments has been discussed.[48]

IN RIVERS AND LAKES

The average content of dissolved substances in river water is of the order of 0·1 – 0·2 g./l. and the Cl content is some 5% of this, but there are very wide variations in these figures. Thus for the Mahanuddy near Cuttack, India, the Amazon at Obidos, Brazil, the Mississippi at New Orleans and the Pecos River in New Mexico, the Cl contents are approximately 2,3,10 and 538 p.p.m. respectively.[49]

Lake waters show even wider variation. Thus the Lac de Champex, Canton Valais, Switzerland shows only about 3 p.p.m. of Cl, while Searles Lake, California contains 4·7% of potassium chloride and 16·35% of sodium chloride.[49]

IN SPRINGS AND NATURAL WATERS

The literature is extremely voluminous, the recorded analyses running into thousands.[50] Among these waters, those containing chloride as the principal anion are perhaps the most conspicuous group. Waters of this class are very common and the range of Cl contents is very wide. Thus the water from the Marienquelle, Bavaria, contains about 0·16% Cl while the brine from a deep well at Conneautsville, Pennsylvania contains some 18% Cl.[50] Some new analyses of the mineral waters at Saratoga, New York, which contain about 0·3% Cl, have been used in deducing a new theory of their origin.[51]

IN PLANTS AND PLANT PRODUCTS

In plants, chlorine exists only as inorganic chlorides dissolved in the cell liquids.[52] Generally, its concentration increases from the roots to the leaves, and usually it is present only in low concentrations in the epidermis, the hair system, flowers, pollen and woody tissue. On the contrary, it is abundant in fleshy roots and rhizomes. Plants which grow in rich or in brine-containing soils contain more chlorine than those grown in poor and dry soils moistened with soft water.[52]

There are considerable variations in concentration from plant to plant, and even within the same kind of plant. Thus the chlorine concentration for the potato, carrot and tobacco has been given as 0·03%, 1·5% and 2·3% respectively, while in clover, values of 0·07 – 0·48% of the dry weight have been recorded. Few plants have been found to contain only very low concentrations of chloride; among these are certain conifers, mosses and brackens[52]. A summary of the more recent determinations is given in Table I.

TABLE I. - CHLORINE CONTENT OF PLANTS AND PLANT PRODUCTS

Reference	Material	Cl content, per cent.
53	TOBACCO: Surinam	Av. 1·98
54	Spanish	>1
55	Spanish	1 –> 2·5
56	Puerto Rican	0·90 – 1·55; av. 1·00
57	Kentucky, Burley var.	0·02 – 1·50
57	Dark var.	0·04 – 2.99
58	FLOWERING PLANTS: *Lycium berlandieri* (Texas)	6·80
58	*Celtis mississippiensis* (Texas)	0.173
58	*Prosopis juliflora* (Texas)	0·674 – 1·31
59	SEEDS: *Plantago psyllium* (Spain)	0·05
60	Yeheb (E. Africa)	0·0196
61	Wheat (U.S.A.)	0·055
61	Wheat flour (U.S.A.)	0·051
62	Wheat flour (Hungary)	0·0602 – 0·0738
63	DATE PALMS: *Phoenix dactylifera* Pinnæ	0.104 – 0·647
63	Fruit pulp	0.158 – 0·694
64	WINES:	0·017 – 0·78 mg./litre.

IN ANIMALS

Chlorine is widely distributed in the animal body in a great range of concentrations. The average chlorine content of the human body is given as 0.45% of the dry weight.[65] Human liver may contain 0·025% and stomach mucus 0·093% of chlorine.[52] The distribution of chlorine in a great number of animal tissues has been studied. For human skin, a figure of 0·283 ± 0·017% Cl has been obtained,[66] whilst average values of 0·86, 0·85, 0·60 and 0·66% Cl have been found for horse, cow, pig and dog skins respectively;[67] in the investigation no connexion was found between sex, age or diet and the chlorine content of the skin.

Refs. p. 268

An enormous number of determinations has been made of the chlorine content of blood, typical figures for man being 0.188% Cl for corpuscles,[68] 0·373% for plasma[68] and 0·203 – 0·250% for plasma from patients suffering from a variety of diseases.[69] Values of 0·037 – 0·094% Cl have been obtained for human saliva.[70] In a study of the distribution of electrolytes in the cerebrospinal fluid of animals and man,[71] figures of 0·443, 0·384 and 0·404% Cl were obtained for man, cattle and dogs respectively. For human colostrum, a figure of 0·088% Cl has been returned.[72]

The chlorine content of goose feathers is given as 0·176 – 0·609%.[73] The form in which chlorine is found in animals is still a very controversial subject. Until 1927 it was though to exist only as chlorides but since then[74] the existence of chlorine-carbon compounds in animal matter has been debated.

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THE PREPARATION OF CHLORINE.

Since the original treatise was written, little study has been made of new methods of making chlorine in the laboratory, partly because the older laboratory methods are fairly satisfactory, but probably mainly because commercial liquid chlorine in conveniently small cylinders is now generally available and is usually pure enough for ordinary laboratory work. For researches requiring specially pure chlorine, commercial chlorine may be purified, or chlorine may be made by one of the older laboratory methods and then purified. In the following sub-section, methods adopted in the last thirty years for the laboratory preparation of very pure chlorine are summarized and, since no analytical details of purity are given, an attempt is made to estimate the degree of purity actually achieved.

PREPARATION IN THE LABORATORY

Pure chlorine can be made at the rate of about 50 l. per hour in simple glass apparatus by the action of hydrochloric acid on an alkali chlorate.[1] For work on the photosynthesis of hydrogen chloride, chlorine was prepared by the action of pure hydrochloric acid on potassium permanganate; the gas was then purified by washing with aqueous permanganate solution, followed by washing with water in darkened vessels and drying over phosphorus pentoxide. The crude chlorine so obtained, after liquefaction, was distilled four or five times, with rejection of the initial and final fractions in each distillation. The final product was left in the solid state until required.[2] The degree of purity to be expected in such chlorine is discussed below. For similar work on the interaction of hydrogen and chlorine, chlorine has also been made by electrolysis, either of pure hydrogen chloride solution or of a saturated solution of cupric chloride which had been boiled under reflux with chlorine for 50 hours in an all-glass apparatus: the electrodes used were of iridium, and the chlorine produced was liquefied and then distilled, head and tail fractions being rejected.[3]

THE LABORATORY PURIFICATION OF COMMERCIAL CHLORINE

As will be pointed out in the sub-section dealing with the commercial preparation of chlorine, there is very little information available in the literature on the quality of commercial material, and there appears to be no internationally accepted specification. Chlorine is manufactured in a variety of ways, and it is to be expected that each process will give its own range of impurities. It is, therefore, not possible to state what impurities are likely to occur in any particular cylinder of liquid chlorine. Impurities actually found, in amounts totalling about 0·2%, were hexachloroethane, carbon tetrachloride, chloroform, bromine and ferric chloride,[4,5] while carbon dioxide, hydrochloric acid, oxygen, carbon monoxide, nitrogen and hydrogen have also been reported.[6] No information is given, however, as to the process by which the chlorine was made, and other impurities may obviously be found in other cylinders of the liquid. Traces of nitrogen trichloride may be present in chlorine made by the electrolysis of brine containing small amounts of ammonia[7] and air has also been found in commercial chlorine.[8] If, however, the chlorine is vaporized from a cylinder, it seems likely that most of the air present would be found in the first portion of the gas to be withdrawn. It is clear, therefore, that whilst commercial chlorine may be satisfactory for some laboratory purposes, it must be specially purified for any precise work, and the following information is available on methods used to effect this purification

Carbon dioxide, hydrochloric acid, oxygen, carbon monoxide, nitrogen and hydrogen can readily be removed by distillation, as was established by absorption of the gas in mercury in a Winkler burette and by passing the gas over purified charcoal at 1150°C. and confirming that there was no loss in weight of the charcoal.[6] The commercial material can also be purified from hydrogen by first drying the gas with sulphuric acid and then passing it over activated birch charcoal at 180 – 200°C., the hydrochloric acid formed being absorbed in water.[9]

Chlorine required specially pure, *e.g.*, for photochemical work, has been prepared by fractionating the commercial material. Thus in work on the formation of carbon tetrachloride from chloroform and chlorine in the presence of light, cylinder chlorine made by I. G. Farbenindustrie A.- G. in Germany was distilled several times under vacuum, and the product was then considered to be free from oxygen, water and hydrochloric acid.[10] A similar purification technique was followed in other photochemical work[2,11,12] whilst in a recent paper[13] details are given of a laboratory distillation column and procedure.

A low pressure sublimation-crystallization procedure has also been used, and it is pointed out that commercial chlorine treated in this way gives higher rates of photochemical reaction with carbon monoxide than similar chlorine distilled in a multiple-plate column[14] and is, therefore, presumably of a higher degree of purity.

THE PURITY OF THE CHLORINE

In none of the papers referred to above are detailed analyses given of the purified chlorine and, in the absence of information as to the quality of the starting material, it is not possible to make an exact estimate of the degree of purity achieved. It is known, however, that large-scale distillation of commercial material can give chlorine of 99·99% purity[4,5] and it appears likely that in the laboratory purification processes, designed to eliminate materials both more and less volatile than chlorine, final products of even higher purity than this may be obtained.

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THE MANUFACTURE OF CHLORINE

OUTPUT

Chlorine ranks with sulphuric acid, sodium hydroxide, sodium carbonate, ammonia, phosphoric acid and nitric acid as one of the most important tonnage chemicals now made, and production has shown a remarkable increase in the past 30 years as indicated by the following Table in which the outputs given in a recent paper[1] have been converted to British tons per year: these units are used throughout this section.

TABLE II. - WORLD PRODUCTION OF CHLORINE[1]

Year	Output in tons per year × 10^{-5}
1919	1·5
1929	3·9
1935/6	6–7
1948	22–24
1949	25–26
1950	30
1951	38

As is shown in the chapter on the uses of chlorine, this tremendous increase in output, about 25-fold in 30 years, has arisen from the development of new uses for the element, particularly in solvents, plastics and intermediates. The productions by countries for the year 1951 are set out in Table III.[1]

TABLE III. - PRODUCTION OF CHLORINE IN VARIOUS COUNTRIES IN 1951[1]

Country	Output in tons × 10^{-3}
U.S.A.	2235
Gt. Britain	345 (not known -
Germany {West	252 estimated)
East	124
France	128
Japan	128
Canada	94
Sweden	74
U.S.S.R.	69
Italy	49
Netherlands	30
Argentina	19
Norway	18
Finland	17
Austria	13
Belgium	12
Spain	11
Switzerland	10
China	10
Czechoslovakia	10
All Others	42·5
Total	3691

METHODS OF MANUFACTURE

Chlorine is made mainly by the electrolysis of brine in diaphragm and mercury cells. A small proportion of the output is obtained by the reaction between sodium chloride and nitric acid, and as a by-product from the manufacture of sodium by the electrolysis of fused sodium chloride. The percentage of chlorine made by these routes during the last 10 years in the United States of America, Germany and Canada, three of the chief manufacturing countries, is shown in Table IV.

TABLE IV. - PERCENTAGE OUTPUT OF CHLORINE MADE BY VARIOUS METHODS

Country	Year	Electrolysis of Brine in		Electrolysis of Fused Sodium Chloride	Nitric Acid/ Salt Process	Ref.
		Diaphragm Cells	Mercury Cells			
Germany	1942	41	59	nil	nil	2
U.S.A.	1946	88·6	4·3	5·8	1·3	2
U.S.A.	1949	←——94——→		←——6——→		3
Canada	1949	-	70	-	-	4
U.S.A.	1950 (est.)	84	7	8	1	4
U.S.A.	1953 (est.)	78·6	14·5	5·7	1·2	5

It may be noted that both in Germany and in Canada the mercury cell process is the favoured route and, on the other hand, about 80% of the vast U.S.A. output of chlorine is by the electrolysis of brine in diaphragm cells, although even in the U.S.A. the proportion of chlorine made in mercury cells has been increasing in recent years.

An account will now be given of the processes for the electrolysis of brine and salt and of the production of chlorine from nitric acid and salt. In the descriptions which follow, more emphasis is given to the theoretical principles which underlie the processes than to practical details of plant items, for information on which reference books on technology may be consulted. Similarly, reference is made to the extensive patent literature only when this is necessary to illustrate new plant principles.

In addition to these main methods for producing chlorine, there are other processes such as the electrolysis of hydrochloric acid and the oxidation of hydrochloric acid which have been used locally. These less important methods are dealt with briefly after the descriptions of the main processes.

THE ELECTROLYSIS OF BRINE IN DIAPHRAGM CELLS

In the original Treatise (Mellor, II, 35), a short description was given of this process which, as shown above, produces over half of the world's output of chlorine. Concentrated sodium chloride solutions are electrolyzed giving chlorine at the anode, hydrogen at the cathode and alkaline brine near the cathode; by means of a diaphragm separating the anode and cathode compartments, the chlorine is kept apart from the hydrogen and alkaline brine. The cell products are thus chlorine, hydrogen and brine containing sodium hydroxide. The total reaction may be represented:-

$$NaCl + H_2O \rightarrow NaOH + \tfrac{1}{2}Cl_2 + \tfrac{1}{2}H_2$$

If the sodium chloride and sodium hydroxide solutions are assumed to be of unit molality, and the other substances in their standard states, it may be calculated from the data given by Rossini *et al.*[6] that at 25°C. $\Delta G_0 = +50{\cdot}445$

kg.-cal./mole and hence that under these conditions the reversible voltage of the cell is 2·19 V. This figure is close to the approximate estimate of reversible voltage, 2·3 V., made over thirty years ago by Moore.[7] In practice the operating voltage of the cell is over 3 volts and the reason for this may be appreciated after a description of the cell has been given.

A large number of different types of diaphragm cells are in operation and installed capacities in U.S.A. of some types for 1946 are given in Table V.[2]

TABLE V. - DIAPHRAGM CELL PLANTS IN U.S.A.
INSTALLED CAPACITY IN 1946[2]

Diaphragm Cell Type	No. of Installations	Total Capacity Tons of Chlorine/ Year × 10^{-3}
Hooker-S	24	438
Hooker Columbia	3	172
Dow-Bipolar	3	248
Vorce	4	135
Gibbs	3	83
Diamond	2	81
Allen-Moore - LeSueur-KML	5	58
Wheeler	3	21
Hargreaves Bird	3	10
Nelson	1	7
Larcher	1	4
Townsend	1	2
MacDonald	1	0·7

The Billiter cell was the main contributor to the 167,000 tons of chlorine made in diaphragm cells in 1942 in Germany but it has been stated that the Billiter cell is not considered to be as satisfactory as the Hooker cell.[2] Brief descriptions of the above cells have recently been given.[8] There are many differences in the design of these cells, particularly in the method of arrangement of the diaphragm, but the essential features are the same in each case and it is proposed to illustrate the whole process by reference mainly to the Hooker-S cell which, as shown in the above Table, is by far the most popular cell in the U.S.A. the chief chlorine-producing country.

PURIFICATION OF BRINE FOR ELECTROLYSIS

Since the processes have much in common, the purification of brine both for diaphragm and for mercury cells is described here.

Common salt is never found in a pure state in Nature, the main impurities being calcium, magnesium and sulphate.[2,9-11] The salt for use in electrolysis is either brought to the factory as the solid[10] or is dissolved underground and delivered by pipeline.[12] Typical analyses for rock salt intended for chlorine production after purification are given in Table VI.

TABLE VI. - COMPOSITION OF RAW SALT

Constituent	Percentage in salt from			
	Brazil	Germany		Italy
NaCl	99·40	96·76	98·00	99·46
Ca	0·09	0·21	0·31	0·10
Mg	0·01	0·01	0·01	0·021
SO_4^{--}	0·27	0·52	0·55	0·16
H_2O	-	2·30	0·14	0·15
Reference	11	10	10	13

The brine to be used in electrolytic cells has to conform to certain standards of purity. For diaphragm cells the content of impurities has to be kept low to reduce the frequency with which the diaphragm becomes blocked, and thus it is essential that the calcium and magnesium concentrations are reduced to the point at which there is no precipitation of lime and magnesia in the presence of the caustic soda which diffuses from the cathode to the anode compartment; heavy metal concentrations must also be kept low to avoid contamination of the caustic soda produced. To reduce corrosion of the anodes the concentration of sulphate should be kept low, say down to 3 - 5 g./litre.[2]

In the mercury cell process it is not customary to remove calcium as, at the concentration normally found, it does not appear to be electrodeposited with the sodium. Magnesium and heavy metals such as iron must, however, be removed since, as will be shown later, they facilitate the discharge of hydrogen at the cathode and also cause the formation of a mercury emulsion known as 'thick mercury'.[2] The permissible concentration of sulphate is about the same as for diaphragm cells, viz., 3 - 5 g./litre.[2]

In both the diaphragm and mercury cell processes, only a portion of the sodium chloride in the brine is electrolyzed at each passage of the brine through the cell, and the remainder is re-used in making up fresh brine.

Methods have been described for the removal of calcium, magnesium and sulphate from brine to be used in electrolysis, using a barium salt such as the chloride together with sodium hydroxide and sodium carbonate.[13,14] The use of such materials as starch, soluble starch, dextrin and glue to increase the settling rate of the magnesium hydroxide precipitated by means of sodium hydroxide and sodium carbonate has also been described.[15] Lime and sodium carbonate have also been used for the purification.[16] Mathematical analysis of the results of the purification of brine containing calcium and magnesium showed that the most satisfactory precipitation was obtained at 15 - 30°C. with sodium hydroxide and sodium carbonate; some of the precipitate from earlier runs should be added to the mixture to provide centres of crystallization.[17] Settling followed by decantation or filtration gives brine of the required purity. Details have been given of brine purification in modern cell plants[13,18-20] and the figures given in Table VII may be taken as representative of brines used as feed for either diaphragm or mercury cells in German plants[19] or for other mercury cell plants,[13] iron and other heavy metals having been removed in the process.[18]

TABLE VII. - COMPOSITION OF SODIUM CHLORIDE SOLUTION FOR ELECTROLYSIS IN DIAPHRAGM OR MERCURY CELLS

Constituent	Per Cent. by weight in Brine for	
	German Diaphragm or Mercury Cells[19]	Other Mercury Cells[13]
NaCl	25·8	Approx. 26
Na_2CO_3	0·019	-
NaOH	up to 0·0084	-
Na_2SiO_3	0·0014	-
Ca	<0·0003	<0·10
Mg	<0·0001	<0·008
Fe	-	<0·0001
SO_4^{--}	-	<0·25

THE PROVISION OF ELECTRICAL ENERGY

As shown above, the present annual world production of chlorine is about

4 million tons and as will be shown later the d.c. electrical energy consumed per ton of chlorine made is around 3000 kw.hr. This large annual direct current requirement of about 10^{10} kw.hr. - more than twice the total electrical energy used in the London area during the year ended 31st March, 1952[21] - is met by the conversion of a.c. energy by rectifiers, rotary converters, or motor generator sets.[22-26] A new type of contact rectifier for which a conversion efficiency of 97% is claimed has been described.[18,27] The d.c. energy is produced at voltages dependent on the number of electrolytic cells to be employed in the series and voltages as high as 700 - 850 are in use.[18,26] Electrical layouts for large electrochemical installations have been described[26] as well as the safety precautions to be observed in the cell room.[28,29]

THE CELL

Size

Electrolytic cells generally have tended to increase in size and the development of the Hooker Type S cell is no exception to this rule.[30] This cell was originally designed to run at 6000 amperes but as the capital costs of the cell have increased the current density has risen and the same cell, which is roughly cubical in structure with sides about 5 ft. in length,[2] has been operated at 10,000 and even 12,000 amperes. Estimates have been made[30] showing that in plants with outputs above about 50 tons per day chlorine would be more economically made in 20,000 ampere cells and thus the Hooker Type S3 has been designed with twice the active electrode areas of the Type S cell. Development is proceeding still further, as is evidenced by a recent report mentioning a still larger cell, the Hooker Type S3A, which is being operated at 30,000 amperes.[31]

Main Features

A diagram showing the main features of the 8,000 ampere Hooker Type S cell based upon information recorded in a recent paper[32] is given in Fig. 1.

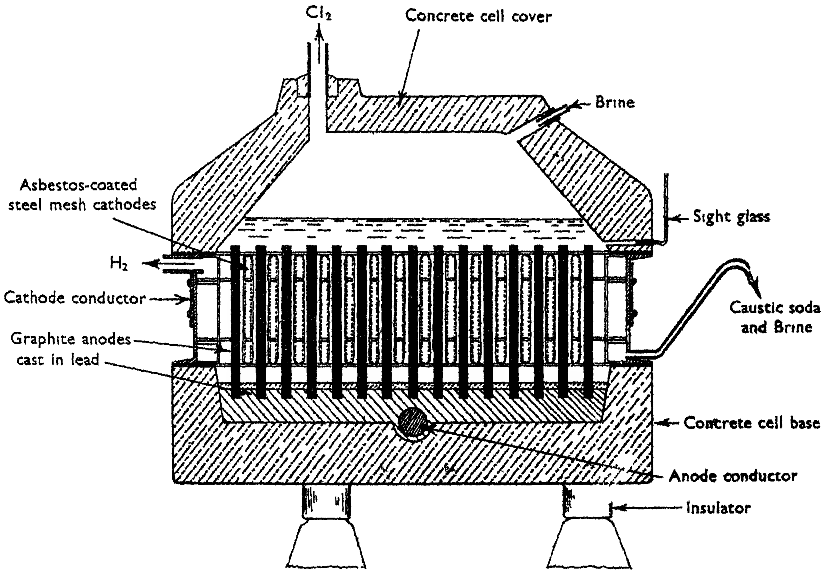


Fig. 1. HOOKER TYPE S DIAPHRAGM CELL

The cell has a concrete cover and cell base. The graphite blades serving as anodes are supported vertically in lead cast in the concrete base; in the case of the Type S cell there are 90 such anodes each 46 × 16 × 3 cm.[33] The cathodes of flat steel wire mesh extend inwards from two sides of a rectangular channel frame so as to fit between the rows of anode blades. The cast lead forming the conductor to the anodes is protected from attack by the cell liquor by a coating of concrete. The diaphragm is asbestos fibre deposited on the cathode in a bath under vacuum.[32] The concentrated brine passes into the anode compartment of the cell through the concrete cover, and the chlorine discharged at the anode escapes through the cell cover. The brine then passes through the asbestos diaphragm while the hydrogen discharged at the steel cathode and the weak brine containing caustic soda escape through the hollow rectangular channel frame at the sides. By maintaining a head of brine between the anode and cathode compartments safe and satisfactory separation of the anode and cathode products is effected. The diaphragm has to be changed after it has become blocked with impurities to such an extent that the brine level in the anode compartment is 25 cm. above the top of the cathode.[33]

Operation

The brine, saturated with sodium chloride at 60°C. and fed to the cell at 75°C., contains about 324 g./l. of sodium chloride and has a specific gravity of 1·210 at 20°/15·5°C. (26·8 g. sodium chloride per 100 g. of solution).[30] Electrolysis is carried out in the Type S cell at an anode current density of about 0·07 amp./sq.cm.[33] The brine feed rate is adjusted so that about 50% of the salt is electrolyzed in its passage through the cell, giving a cell exit liquor containing sodium chloride and sodium hydroxide in the weight ratio 1·35 : 1. The treatment of this liquor, to give pure caustic soda for sale and salt for return to the cell, is described below.

Energy Consumption

Data for the energy used in both the type S and type S3 cells have recently been given[31-33] and the figures in the following tables are based on this information, those for energy consumption per ton of chlorine being obtained from the published voltages and current efficiencies.

TABLE VIII.- ENERGY CONSUMPTION IN THE DIAPHRAGM CELL PROCESS

	Data for Hooker Type S Cells					
Anode current density amp./sq.cm.	0·055	0·074	0·092	0·111	0·129	0·148
Cathode current density amp./sq.cm.	0·050	0·066	0·083	0·099	0·116	0·132
Cell current (Amperes)	6,000	8,000	10,000	12,000	14,000	16,000
Average Cell Temperature °C.	80	87	92	95	97·5	99
Chlorine per cell per day: British tons	0·177	0·239	0·302	0·363	0·425	0·488
Average cell voltage	3·26	3·48	3·72	3·94	4·14	4·35
Current Efficiency per cent.	94·7	96·0	96·8	97·3	97·7	98
Energy Consumption kw.hr./ British ton of chlorine	2644	2784	2952	3110	3255	3410
Approx. Energy Efficiency, %.	64	60	57	54	52	49

It is not possible to use these figures for current efficiency and voltage to calculate the exact energy efficiencies for the process, because no results have been published for the reversible voltage of the cell determined under actual operating conditions. However, approximate figures may be obtained by using as a reference 2·19 V., the reversible voltage under standard conditions at 25°C. (see page 274). This means that one ton of chlorine

TABLE IX. - ENERGY CONSUMPTION IN THE DIAPHRAGM CELL PROCESS

		Data For Hooker S-3 Cells				
Anode current density amp./sq.cm.	0·055	0·074	0·092	0·111	0·129	0·148
Cathode current density amp./sq.cm.	0·050	0·066	0·083	0·099	0·116	0·132
Cell Current (Amperes)	12,000	16,000	20,000	24,000	28,000	32,000
Average Cell Temperature: °C.	86	91	95	96·9	98·6	100·0
Chlorine per cell per day: tons	0·354	0·478	0·603	0·727	0·850	0·975
Average Cell Voltage	3·20	3·43	3·65	3·87	4·08	4·27
Current Efficiency: %	94·7	96·0	96·8	97·3	97·7	98·0
Energy Consumption: kw.hr. per ton of chlorine	2,596	2,744	2,896	3,055	3,208	3,347
Approx. Energy Efficiency, %	65	61	58	55	53	50

theoretically requires 1682 kw.hr. of energy and the energy efficiencies in the above tables have been calculated on this basis.

Voltage

It was pointed out above that, under the standard conditions described, the reversible voltage for the cell at 25° is 2·19 V. The reasons for the much higher voltage in the working cell are:

(*a*) there are high overvoltages of chlorine and hydrogen at anode and cathode respectively;

(*b*) there are potential drops through the electrolyte gap, through the diaphragm, through the anode and cathode leads and through the various contacts.

Each of these factors will now be dealt with in turn.

Measurements have been made of the chlorine discharge potential[34] in sodium chloride solutions. The results for graphite, magnetite and platinized platinum are set out in Table X.

TABLE X. - CHLORINE DISCHARGE POTENTIALS IN SODIUM CHLORIDE SOLUTION (260 g./l.) AT MAGNETITE, ACHESON GRAPHITE AND PLATINIZED PLATINUM ELECTRODES[34]

Electrode Material	Magnetite			Acheson Graphite				Platinized Platinum		
Temp. °C.	25	50	75	16	25	50	75	25	50	75
Current Density amp./sq.cm.	Discharge Potentials in Volts									
0·01	1·85	1·75	1·74	1·47	1·43	1·38	1·33	1·36	1·34	1·34
0·02	1·90	1·80	1·79	1·55	1·49	1·44	1·35	1·37	1·35	1·35
0·03	1·95	1·84	1·82	1·59	1·52	1·47	1·38	1·37	1·35	1·35
0·04	1·98	1·87	1·87	1·61	1·55	1·48	1·40	1·38	1·36	1·35
0·05	2·01	1·90	1·90	1·63	1·58	1·50	1·42	1·38	1·36	1·35
0·06	2·04	1·92	1·91	1·65	1·61	1·51	1·44	1·39	1·36	1·36
0·07	2·1	1·94	1·92	1·67	1·64	1·52	1·45	1·39	1·37	-
0·08	2·12	1·96	1·93	1·70	1·66	1·53	1·46	1·40	1·38	-
0·09	-	1·99	1·94	1·72	1·68	1·54	1·47	1·40	1·38	-
0·10	-	2·01	1·95	-	1·70	1·55	1·48	1·41	1·39	-

No determinations have been reported of chlorine discharge potentials at the temperatures of 80 - 100°C. or at the highest current densities prevailing in the Hooker Type S cells but it is possible to obtain approximate results by extrapolating the figures for Acheson graphite in Table X as regards both temperature and current density. Chlorine discharge ptoentials of about 1·37 and 1·48 V. are thus obtained at 90°C. and at 0·05 and 0·15 amp./sq.cm.

respectively, the two limits in the current density range in Tables VIII and IX. The reversible electrode potential of chlorine at 25°C. is 1·3595 V.[35] Hence in the working cell the anode potentials are 0·01 – 0·12 V. above the standard electrode potential.

In addition to the figures given in Table X determinations have been made[36] of the discharge potential of chlorine on platinized platinum and on three different types of graphite. The values, reported as the mean of several hundred determinations at 50°C. ± 0·3°, are set out in Table XI.

TABLE XI. - CHLORINE DISCHARGE POTENTIALS IN VOLTS AT 50°C. IN 22% SODIUM CHLORIDE SOLUTIONS[36]

Current Density amp/sq.cm.	Platinized Platinum	Acheson Graphite	Siemens Graphite	IG Graphite
0·1	1·423	1·427	1·433	1·438
0·24	1·494	1·531	1·570	1·550

The values for a current density of 0·1 amp./sq.cm. are considerably lower than those of Stender.[34]

The hydrogen discharge potential has been determined for various ferrous metal cathodes in a sodium hydroxide – sodium chloride solution of about the same composition as that occurring in the cathode compartment of the cell.[34] No figures are available for 90°C. but for the purpose of this discussion it is probably sufficiently accurate to use the figures in Table XII which are for 75°C.

TABLE XII. - HYDROGEN DISCHARGE POTENTIALS IN VOLTS IN NaOH (2N) + NaCl (2·9N) SOLUTION AT 75°C.[34]

Electrode C.D. amp/sq.cm.	Roofing Iron	Sample of Soft Iron Cathode	Steel	Vorce Cathode (Sample No. 1)	Cast Iron	Vorce Cathode (Sample No. 2)
0·005	0·96	1·09	1·03	1·03	1·14	-
0·010	1·03	1·12	1·09	1·09	1·22	1·17
0·020	1·13	1·17	1·13	1·13	1·33	1·20
0·030	1·17	1·21	1·15	1·15	1·39	1·22
0·040	1·21	1·25	1·17	1·17	1·44	1·24
0·050	1·25	1·29	1·19	1·19	1·47	1·26
0·060	1·28	1·33	1·21	1·20	1·50	1·27
0·070	1·32	1·37	1·23	1·21	-	1·29
0·080	1·36	1·41	1·25	1·22	-	1·30
0·090	1·40	1·45	1·27	1·24	-	1·31
0·100	1·43	1·48	1·28	1·25	-	1·31

The figures for steel, the material of the cathode in the Hooker Type S cell, may be extrapolated to give a hydrogen discharge potential of 1·33 V. at a current density of 0·13 amp./sq.cm., the highest value considered in the above energy consumption tables. Discharge potentials of 1·19 – 1·33 V. thus apply over the current density range considered above; this contrasts with the reversible hydrogen potential at 25°C., in sodium hydroxide solution of unit molality, of 0·828 V.[37]

No figures have been published for Hooker Type S cells for the potential drops in the electrolytes in the anode and cathode compartments, in the diaphragm, in the anode and in the contacts. However, measurements on the Vorce cell[34] operated at 1,000 amp. give these as 0·403, 0·145, 0·100 and 0·10 V. respectively, which may serve to define the order of the quantities.

It is thus seen that the divergence between the theoretical and the working voltage in a diaphragm cell, something over one volt, can be explained on the basis of the additional potential drops dealt with above.

It is clear that a considerable saving in electrical energy would result if anode and cathode materials could be found with lower chlorine and hydrogen overvoltages respectively. However, the problem is difficult, particularly in the case of the anode which must have high resistance to the very corrosive chlorinated brine. The various possibilities are considered below (see page 286)..

The potential drop in the electrolyte depends on the current density, on the width of the inter-electrode gap, and on the conductivities of the solutions in the anode and cathode compartments, which in turn depend on their concentration and temperature. On account of the magnitude of the energy loss from this cause, much attention has been paid to designing the cell with the minimum practicable working distance between the electrodes.[38] Since the inter-electrode gap increases as the anodes wear (see page 287) a reduction in anode wear is important as a means of saving energy. The importance of the energy quantities involved is shown by the figures given in Tables XIII and XIV which are derived from measurements made on the conductivity of solutions of sodium chloride[39,40] and of mixed solutions of sodium chloride and sodium hydroxide[41] respectively.

TABLE XIII. - POTENTIAL DROP IN SOLUTIONS OF SODIUM CHLORIDE

g.NaCl/ 100 g. Solution	Potential drop in volts through 1cm. of Solution at Current Density of 0·1 amp./sq.cm.					
	40°C.	50°C.	60°C.	70°C.	80°C.	100°C.
5	$1{\cdot}02_0$	$0{\cdot}88_5$	$0{\cdot}78_1$	$0{\cdot}69_4$	$0{\cdot}62_5$	$0{\cdot}48_3$
7·5	$0{\cdot}69_4$	$0{\cdot}60_2$	$0{\cdot}53_5$	$0{\cdot}47_4$	$0{\cdot}43_0$	$0{\cdot}33_7$
10	$0{\cdot}54_1$	$0{\cdot}47_2$	$0{\cdot}41_3$	$0{\cdot}36_8$	$0{\cdot}33_4$	$0{\cdot}27_0$
12·5	$0{\cdot}45_5$	$0{\cdot}39_7$	$0{\cdot}34_8$	$0{\cdot}31_2$	$0{\cdot}28_2$	$0{\cdot}23_0$
15	$0{\cdot}40_2$	$0{\cdot}34_7$	$0{\cdot}30_7$	$0{\cdot}27_4$	$0{\cdot}24_7$	$0{\cdot}20_0$
17·5	$0{\cdot}36_4$	$0{\cdot}31_4$	$0{\cdot}27_7$	$0{\cdot}24_8$	$0{\cdot}22_3$	$0{\cdot}18_0$
20	$0{\cdot}33_8$	$0{\cdot}29_2$	$0{\cdot}25_5$	$0{\cdot}22_6$	$0{\cdot}20_6$	$0{\cdot}16_6$
22·5	$0{\cdot}31_8$	$0{\cdot}27_4$	$0{\cdot}23_9$	$0{\cdot}21_3$	$0{\cdot}19_2$	$0{\cdot}15_3$
25	$0{\cdot}30_2$	$0{\cdot}26_0$	$0{\cdot}22_6$	$0{\cdot}20_1$	$0{\cdot}18_1$	$0{\cdot}14_2$

TABLE XIV. - POTENTIAL DROP IN MIXED SOLUTIONS OF SODIUM CHLORIDE AND SODIUM HYDROXIDE

Concn.,g./100g.soln.		Potential drop in volts through 1 cm. of solution at current density of 0·1 amp./sq.cm.					
NaCl	NaOH	40°C.	50°C.	60°C.	70°C.	80°C.	90°C.
21·49	4·11	0·27	0·23	0·20	0·17	0·15	0·13
16·91	7·92	0·25	0·21	0·18	0·15	0·14	0·12
9·21	14·00	0·21	0·18	0·15	0·13	0·12	0·10
6·32	16·40	0·21	0·18	0·15	0·13	0·11	0·10

It should be borne in mind that in a working cell the solutions in the anode and cathode compartments must be saturated with chlorine and hydrogen respectively, and contain a dispersion of bubbles of these gases. The potential drop through the electrolyte includes not only the resistance arising from this cause but also the resistance set up by the bubbles of gas liberated at the electrode surfaces. No measurements have been published of these separate effects but this point is discussed for the mercury cell, where the gas bubble effect at the anode is much larger since the chlorine is in that case discharged on the underside of horizontal graphite plates.

The potential drop in the diaphragm is also an important item of cost and this is dealt with later (see page 289).

The electrical resistances through the anode and cathode leads are a function of the cell design and as shown above represent only about 2 – 3% of the total energy expenditure. Theoretically, a potential difference should exist at the diaphragm, where the anolyte of sodium chloride is in contact with the catholyte consisting of a mixture of sodium chloride and sodium hydroxide solutions. No figures have been published for this potential difference but it is thought to be small.[2] This opinion is borne out by data on liquid junction potentials recently published[42] from which it appears that this potential difference in the diaphragm cell must be only of the order of millivolts and thus negligible.

Current Efficiency

The current efficiency is the ratio, expressed as a percentage, of the weight of the actual products of electrolysis to the weight that might theoretically be liberated by the quantity of electricity used. Thus with chlorine cells one Faraday, 96,484 absolute coulombs, theoretically liberates 35·457 g. of chlorine and 40·005 g. of sodium hydroxide, or in technical units 1000 ampere hours should give 2·916 lb. of chlorine and 3·290 lb. of sodium hydroxide. In practice, only the sodium hydroxide is weighed, as the chlorine produced is more difficult to measure, but recently a method of determining current efficiency in diaphragm cells by gas analysis has been published.[43] In the discussion which follows it is assumed that the chlorine or anodic current efficiency is the same as the cathodic or sodium hydroxide efficiency, although only a few experiments on this point have been reported.[33]

The weight of cell products is less than the theoretical value for the following reasons:

(1) There may be leakages of current to earth, or current may pass from anode to cathode non-electrolytically, e.g., over the outside of the cell casing, or between the electrodes if a short-circuit occurs.
(2) Secondary reactions occur at the electrodes.
(3) Secondary reactions occur in both the anode and cathode solutions.
(4) There are always handling losses in the working up of the cell products.

No measurements have been reported on the amount of current which leaks to earth through the cell insulators but the amount is thought[2] to be a small fraction of the other losses. On account of the small potential difference across the cell, non-electrochemical passage of current over the cell casing may be expected to be very small, and losses arising from direct passage of current between anode and cathode should not occur apart from accidental short-circuiting.

Reactions at the Anode

The anodes are now generally of graphite (see page 286) and the main process

$$2\,Cl^- \rightarrow Cl_2 + 2\,e \,\ldots\ldots\ldots\, I$$

takes place under cell conditions as shown above at a potential of + 1·3 to 1·4 V., relative to the hydrogen electrode.

There is evidence that the following reactions also take place:

$$4OH^- \rightarrow 2H_2O + O_2 + 4\,e \,\ldots\ldots\ldots\, II$$
$$4OH^- + C \rightarrow 2H_2O + CO_2 + 4\,e \ldots\ldots III$$

while if sulphate is present in the brine, current is also used to discharge oxygen by a process other than II which has not yet been fully investigated.[44]

Finally, hypochlorite ion present in the brine, from the hydrolysis of chlorine and from reaction of dissolved chlorine with hydroxyl ion diffusing from the catholyte, may be discharged to form chlorate:

$$6\ ClO^- + 3H_2O \rightarrow 2\ ClO_3^- + 4Cl^- + 6\ H^+ + \tfrac{3}{2}\ O_2 + 6\ e \ldots\ldots \text{IV}$$

At first sight, it seems remarkable that hydroxyl ion is discharged from the anolyte at the low pH of about 4 to such an extent as to give proportions of oxygen and carbon dioxide in the cell gas each of the order of 1%. However, the electrode potential for reaction II at 25°C. in a solution of unit molality (of hydroxyl ion) is $E^\circ = 0{\cdot}401$ V.[45] At other hydroxyl ion concentrations the potential is given by

$$E = E_0 - 0{\cdot}0592 \log_{10} (OH^-)$$

and hence at pH 4 is 0·993 V.

Similarly, under standard conditions at 25°C., the potential for reaction III calculated by the author (W.W.S.) from available thermodynamic data[45,46] is − 0·621 V., and at pH 4, − 0·029 V. These potentials are much below the chlorine discharge potentials of 1·3 − 1·4 V. and, therefore, on thermodynamic grounds alone, reactions II and III should proceed to the almost complete exclusion of the normal chlorine-producing reaction I. The fortunate fact that in practice nearly pure chlorine is obtained at the anode, with relatively little oxygen and carbon dioxide, is explained by the existence of a very high oxygen overvoltage at the graphite surface (see page 286). Small proportions of carbon monoxide have also been reported in the cell gas.[33]

The rate at which chlorate is formed by anodic oxidation will depend on the concentration of hypochlorite ion, which in turn depends on the equilibria set up in the reactions: $Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl$, and $HOCl \rightarrow H^+ + OCl^-$. No work has been reported on the determination of these equilibria under conditions resembling those occurring in the anolyte, but the values of the equilibrium and dissociation constants in water at room temperature are so small (see page 283) that at the pH usually prevailing in the anolyte, about 4, only very small concentrations of hypochlorite ion can be present. Thus little chlorate formation at the anode is to be expected.

From reactions I, II and III it follows that the percentage loss in current efficiency through discharge of oxygen and carbon dioxide is equal to twice the sum of the percentages by volume of these gases in the chlorine. In the most extensive recent investigation[33] on factors affecting current efficiency in diaphragm cells, work was done on Hooker S type cells and the findings have therefore a direct bearing on the energy consumption figures given in Tables VIII and IX. The results in Table XV were obtained in operating at anode current densities of 0·069 − 0·100 amp./cm^2., and at a temperature not stated but apparently about 85 − 90°C., according to data reported by Hubbard for cell temperatures at similar current densities.[30] In each case the cell was run under steady conditions for at least ten hours before the measurements recorded in the Table were made. Cell conditions were altered by varying the concentration of sodium chloride in the brine feed (runs 4, 6, 10, 11, 12), the rate of brine feed (runs 7, 10, 11, 12) and the current density (runs 16, 19, 22, 23), and by adding sodium sulphate (runs 14, 22), hydrochloric acid (run 17) and sodium hydroxide (run 13) to the brine feed. Included in the Table are the estimated losses from other factors which will be discussed later. The figures for oxygen and carbon dioxide in the cell gas are exclusive of oxygen from the air and carbon dioxide from carbonate present in the brine, and have been calculated from the published results by the author (W.W.S.) in terms of volumes of gas per 100 volumes of chlorine.

The conclusions reached[33] are that, under normal operating conditions, with 258 g./l. (about 22%) of sodium chloride and 4·4 g./l. of sodium sulphate in the anolyte, and using graphite anodes with an age of 330 – 400 days:

(*a*) the largest loss of chlorine arises from discharge of hydroxyl ion, the loss being proportional to the hydroxyl ion concentration in the anolyte;

(*b*) the loss of current efficiency arising from sulphate in the brine is proportional to the concentration of sulphate, is independent of pH, and amounts to only about 10% of the total chlorine loss when the brine contains 0·38% of sodium sulphate and when the anolyte has the normal pH of about 4;

(*c*) the loss from the discharge of hypochlorite ion to give chlorate at the anode is very small when the anolyte is at its normal pH of about 4 but increases with pH.

Reaction in the Anolyte

There are two main reactions in the anolyte which cause a loss in current efficiency.[33]

(*a*) Chlorine dissolves in the hot brine where it hydrolyses as follows:-

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HClO.$$

However, the equilibrium constant for this reaction is

$$\frac{[H^+][Cl^-][HClO]}{[Cl_2]} = 4{\cdot}66 \times 10^{-4} \text{ at } 25°C.$$

in water[47] and is smaller in concentrated sodium chloride solutions.[48] This means that the loss of chlorine carried by the anolyte into the cathode compartment is low under normal operating conditions as the figures in Table XV show. The loss increases as the pH of the anolyte is raised and reaches 1·3% where alkaline brine was fed to the cell (run 13, Table XV).

(*b*) Hypochlorous acid and hypochlorite ion react to form chlorate ion:

$$ClO^- + 2\,HOCl \rightarrow ClO_3^- + 2\,Cl^- + 2\,H^+.$$

The figures in Table XV show that at the normal pH of about 4 the losses from this cause are usually less than 1% and are very small with acidified brines, as might be deduced from the above constants.

Reactions at the Cathode

The main reaction

$$2\,H^+ + 2e \rightarrow H_2 \,.\,.\,.\,.\,.\,.\,.\,.\,.\,.\, \text{I}$$

occurs at a potential of −1·19 to −1·33 volts as already shown. Chlorine, hypochlorite and chlorate are carried into the cathode compartment in the brine from the anode compartment. The dissolved chlorine will react with the sodium hydroxide to form chlorine and hypochlorite

$$Cl_2 + 2\,OH^- \rightarrow Cl^- + OCl^- + H_2O \,.\,.\,.\,.\,.\,.\,.\,.\,.\,.\, \text{II}$$

and it is stated that cathodic reduction of the hypochlorite and chlorate ion may take place.[33]

These reductions may be set out in the form

$$ClO^- + 2H^+ + 2\,e \rightarrow Cl^- + H_2O \,.\,.\,.\,.\,.\,.\,.\,.\,.\,.\,.\, \text{III}$$
$$ClO_3^- + 6H^+ + 6\,e \rightarrow Cl^- + 3H_2O \,.\,.\,.\,.\,.\,.\,.\,.\,.\,.\, \text{IV}$$

TABLE XV.- CURRENT EFFICIENCY LOSSES IN A HOOKER-TYPE S CELL

Determination	Run No.												
	4	6	10	11	12	7	16	19	22	23	14	17	13
Feed Brine; g.NaCl per 100g. solution	21·85	25·97	26·78	22·68	26·32	25·46	26·74	26·35	24·90	26·70	25·06	23·38	24·60
Feed Brine; g.Na_2SO_4 per 100g. solution	0·22	0·25	0·29	0·21	0·24	0·22	0·39	0·55	3·52	0·61	2·30	0·42	0·23
Anolyte; pH	3·85	4·05	3·95	3·58	3·43	4·45	4·13	3·48	1·48	1·55	3·85	0·72	4·60
Anolyte; g.NaCl per 100g. solution	18·0	22·0	23·0	19·3	22·4	21·0	22·0	22·2	19·4	22·6	20·9	22·6	22·2
Catholyte; g.NaCl per 100g. solution	10·48	13·80	15·52	12·43	15·23	10·86	12·48	14·48	11·78	15·33	13·32	9·35	14·55
Catholyte; g.NaOH per 100g. solution	10·39	11·36	10·09	9·12	9·28	14·55	15·52	11·90	12·58	11·77	11·55	11·58	10·83
Oxygen in Chlorine; vols. O_2 per 100 vols. Cl_2	2·18	1·70	0·45	0·46	0·32	4·55	5·26	1·41	0·35	0·21	1·38	0·29	4·57
Carbon dioxide in Chlorine; vols. O_2 per 100 vols. Cl_2	1·73	1·08	0·98	1·16	0·73	2·50	4·02	1·54	1·36	0·56	1·97	0·24	4·10
% Chlorine current efficiency loss as:													
(1) $O_2 + CO_2$ in Chlorine	7·35	5·34	2·86	3·64	2·24	12·10	15·60	5·59	3·32	1·51	6·25	1·05	14·68
(2) Cl_2 + HOCl in anolyte	0·42	0·41	0·61	0·61	0·46	0·66	0·30	0·24	0·14	0·18	0·38	0·18	1·31
(3) Chlorate in anolyte	0·33	0·18	0·14	0·15	0·07	0·97	4·72	0·75	0·07	0·03	0·17	0·01	5·42
Total, (1) + (2) + (3)	8·10	5·93	3·61	4·40	2·77	13·73	20·62	6·58	3·53	1·72	6·80	1·24	21·41
Measured Loss of NaOH: %	8·50	3·60	2·50	3·30	1·60	14·3	21·0	7·0	3·5	0·5	2·80	-	6·3
% NaOH current efficiency loss as:													
(4) Alkali entering anolyte from catholyte	7·20	5·48	2·28	3·22	1·62	12·51	20·00	6·17	2·22	0·32	5·53	3·36	5·20
(5) Chlorine compounds entering catholyte from anolyte	0·44	0·32	0·48	0·52	0·44	0·40	0·24	0·24	1·04	0·52	0·28	2·48	0·84
Total, (1) + (2)	7·64	5·80	2·76	3·74	2·06	12·91	20·24	6·41	3·26	0·84	5·81	5·84	6·04

and their standard potentials in sodium hydroxide solution of unit molality, calculated by the author (W.W.S.) from the available thermodynamic data,[47] are $E^\circ = -0{\cdot}89$ and $-0{\cdot}62$ respectively. The reactions are therefore possible on thermodynamic grounds but unfortunately no experimental work appears to have been done on them under cell conditions and only few analyses of the catholyte liquor are available from which the extent of the reactions might be deduced (see below).

Reactions in the Catholyte

The discharge of hydrogen ion at the cathode leaves the equivalent amount of hydroxyl ion in the catholyte and losses of this in the cell can occur in only two ways:-

(1) Hydroxyl ion diffuses through the diaphragm into the anode compartment where part is discharged at the anode and part reacts with dissolved chlorine as dealt with above. The pore size of the diaphragm and also the rate of passage of brine from the anode compartment to the cathode compartment are chosen so as to reduce this quantity of hydroxyl ion to the point where a reasonable compromise is reached between maximum current efficiency and maximum concentration of sodium hydroxide in the catholyte;[33] determinations have been made[33] of the loss of alkali in this way and the figures are set out in Table XV. It is clear that diffusion of hydroxyl ions accounts for the major loss of alkali.

(2) Hydroxyl ion is used up by reaction with chlorine, hydrochloric acid, hypochlorous acid, and hypochlorite ion carried in the brine passing from the anode to the cathode compartment. The estimated loss in this way is also shown in Table XV, from which it appears that it is small, being less than 1% except where the cell is fed with very acid brine.

The following reactions may take place between hydroxyl ion and the substances carried into the cathode compartment in the brine from the anode compartment.

$OH + Cl_2 \rightarrow Cl^- + HClO$ I
$OH^- + HClO \rightarrow ClO^- + H_2O$ II
$OH^- + H^+ \rightarrow H_2O$ III
$3ClO^- \rightarrow ClO_3^- + 2Cl^-$ IV

At the high pH of the catholyte, about 14, almost all the hydrogen ion and hypochlorous acid disappear, leaving hypochlorite ion at first the only oxidized form of chlorine. The free energy change under standard conditions at 25°C. for reaction IV calculated by the author (W.W.S.) from the available data[47] is $\Delta G^\circ = -36{\cdot}62$kg.-cal., indicating that at equilibrium the concentration of hypochlorite ion would be negligible. This subject has been considered on general grounds[42] but no experimental work under the conditions which occur in a working cell appears to have been done and no figures for hypochlorite concentrations in the exit catholyte liquor from industrial cells have been reported, although the presence of hypochlorite is implied.[8] However, sodium chlorate concentrations of about 0·19 g./l. (about 0·016 g. ClO_3 per 100 g. solution) have been found[49] in the catholyte liquor from Gibbs diaphragm cells. Such a concentration would explain a current efficiency loss of about 0·4% on the hypothesis that the overall loss of chlorine is by the reaction

$$3Cl_2 + 6NaOH \rightarrow NaClO_3 + 5NaCl + 3H_2O.$$

The conclusion from the above discussion on current efficiency losses in diaphragm cells may be summarized thus:-

(1) nearly all the loss in anodic current efficiency arises from the discharge of hydroxyl ion which has diffused through the diaphragm from the cathode compartment;

(2) the hydrogen current efficiency is nearly theoretical, but there is a loss of the cathode product, sodium hydroxide, approximately equal in magnitude to the loss in anodic current efficiency;

(3) other reactions such as discharge of sulphate, chlorate or hypochlorite, or reactions in the cell to form hypochlorite or chlorate, are normally of minor importance.

Losses in the Handling of Cell Products

No figures have been reported on losses incurred in the handling of the products, but it is clear that a precise knowledge of these losses will depend on the accuracy of the determinations of the weights of the cell products and final products. Loss of some of the gaseous cell products, chlorine and hydrogen, is particularly likely.

The Electrodes

As already pointed out, the choice of materials for the electrodes is important. For economic reasons, not only has corrosion and the consequent need for replacement to be reduced to a minimum but also the chlorine and hydrogen overvoltages must be kept as low as possible to conserve energy.

Anodes

For anodes, graphite now appears to be the only material in commercial use;[8] amorphous carbon, magnetite and platinum, which had been employed in the past,[50] have been superseded. Some twenty years ago, a search for a better material than graphite was made and alloys of lead-silver, mercury-lead, mercury-lead-silver and silver-lead-manganese were tested[50] while the use of platinum was re-examined.[51] More recently, attempts have been made to use iron anodes surfaced with magnetite,[52] iron anodes surfaced with magnetite bearing noble metals such as gold, silver, platinum, palladium, iridium or rhenium,[53] and anodes of silicon carbide or graphite coated with silicon carbide,[54] but there are no reports that any of these came into commercial use. The position of graphite at present therefore seems secure.

It is less difficult to obtain materials suitable for cathodes because the corrosion problem is much less severe than for anodes. Steel appears to be in general use as cathode and the reasons for its choice will be given below.

Graphite as Anode

Graphite has several advantages as an anode. Thus it has fairly good mechanical strength, is of moderate price and has low apparent density and electrical resistivity; it also shows good resistance to corrosion under cell conditions. In addition, as was remarked above, it has a very high oxygen overvoltage which permits the discharge of nearly pure chlorine. On the other hand, as the figures in Tables X and XI show, it has a chlorine overvoltage which leads to an important loss in energy. It is clear that, ideally, the anode material should have a negligible chlorine overvoltage and an oxygen overvoltage so high that no oxygen or oxygen products appear in the cell gas.

The figures given in Table XI for chlorine discharge potentials show that these vary with the grade of graphite and thus that graphite with a lower chlorine discharge potential than any of those reported may perhaps be obtainable.

No determinations of oxygen overvoltage have been made under the conditions which apply in commercial cells. Figures recently available[55] are set out in Table XVI.

TABLE XVI. - OXYGEN OVERVOLTAGES IN VOLTS ON GRAPHITE AND SMOOTH PLATINUM IN N-KOH SOLUTION AT 20°C.[55]

Material	Method	Current Density in amp./sq.cm.					
		0·00001	0·0001	0·001	0·01	0·1	1
Graphite	Direct	0·31	0·37	0·50	0·98	1·17	approx. 20
	Extrapolation to zero time.	0·31	0·37	0·50	0·96	1·12	2·20
Smooth Pt.	Direct	0·52	0·80	1·11	1·33	1·56	2·02
	Extrapolation to zero time.	0·52	0·80	1·11	1·32	1·50	1·55

While it is not possible to predict from the figures in the Table the exact overvoltages which would apply under cell conditions at temperatures of the order of 90°, the figures do indicate that these overvoltages must be high. As shown above, the potential for the reaction $4OH^- \rightarrow 2H_2O + O_2 + 4e$ at pH 4 is + 0·993 V. The current density in a commercial cell is of the order of 0·1 amp./sq.cm. and since the oxygen content of the cell gas is of the order of 1%, the current density for hydroxyl ion discharge is about 0·002 amp./sq.cm. for which, from the results in Table XVI, an over-potential of around 0·5 V. is to be expected. If the over-potential at cell temperature is of this order of magnitude, then the sum of 0 5 and 0·993 V. is close to the chlorine discharge potential and thus the unexpectedly small proportion of oxygen in the cell gas is explained. However, the small proportion of carbon dioxide in the cell gas cannot be explained in this way. As stated above, the carbon dioxide is supposed to result from the reaction

$$C + 4\,OH^- \rightarrow CO_2 + 2\,H_2O + 4\,e$$

the calculated potential for which is only −0·029 V. at pH 4; this reaction is, therefore, much more likely on thermodynamic grounds than the discharge of hydroxyl ion to oxygen. The small extent to which the formation of carbon dioxide actually proceeds is presumably a consequence of the reaction being in this case one between a solid and a gas.

Usage of Graphite

The formation of carbon dioxide during electrolysis and in addition the erosion of particles of graphite which results from this electrolytic attack and from the movement of the brine, mean that the graphite is slowly consumed. Widely varying figures are given for the amount of graphite used per ton of chlorine made. These figures for graphite used include not only the graphite actually consumed in the process but also scrap graphite from the production of the anode and material discarded when the anodes have worn to such an extent that the current density on them, the electrolyte gap between anode and cathode, and consequently the cell voltage, have risen to an uneconomic degree. In two modern reviews[2,8] graphite usages are given of 8 - 9 lb. and of 7 - 28 lb. per ton of chlorine: for Gibbs cells a figure of 14 lb. has been given[49] and for the Billiter cell 17 lb.[56]

Factors influencing the Rate of Graphite Wear

The rate of wear of the graphite in the cell is affected by the current density as well as by the pH, temperature and concentration of the brine in the anolyte compartment. The pH of the anolyte brine depends on the pH of the feed brine and on the amount of hydroxyl ion which diffuses from the cathode compartment, and the latter in turn depends on the efficiency of the diaphragm and on the rate of flow of brine from anode to cathode compartments. In recent laboratory studies[57,58] some of these factors have been examined, while in the current efficiency work described above the effect of pH of the feed brine was examined in a commercial Hooker Type S cell.[33] The main results from the laboratory diaphragm cell are these:-

(1) when other factors are constant, graphite corrosion rate increases by 1·15 - 1·20 g./1000 amp. hr. per 10°C. in the range 50 - 95°C; the relative rates of wear at 50°, 60°, 80°, and 95° are 1 : 1·7 : 3·1 : 4·1;
(2) at constant temperature and current density, increase in brine feed rate and in sodium chloride concentration of the anolyte greatly reduces graphite corrosion rate;
(3) corrosion of graphite in terms of weight loss per 1000 amp. hr. decreases slightly with increasing current density; graphite wear per unit time is, however, approximately directly proportional to current density.

In the work on the Hooker Type S cell (Table XV above) reduction of the pH of the anolyte had a very marked effect in lowering the carbon dioxide content of the cell gas. Thus at pH 0·72 only 0·24% of carbon dioxide was found in the cell gas compared with a figure of about 1 - 2% for normal conditions at a pH of about 4. This means a large reduction in the rate of anode wear to which the authors draw attention. This reduction is to be expected since the rate of the main anode-consuming reaction

$$C + 4\,OH^- \rightarrow CO_2 + 2\,H_2O + 4\,e$$

is presumably proportional to the concentration of hydroxyl ion.

No work appears to have been done on the effect of variation in the quality of the graphite on the rate of anode wear, despite the indication above that chlorine overvoltage, and hence possibly oxygen overvoltage and rate of wear, varies with different graphites.

Impregnation of Anodes

It has been known for many years that impregnation of graphite may reduce its rate of wear when used as anode in the electrolysis of brine. Thus as early as 1919[59] impregnation with various oils was described, and it was pointed out that, to avoid the presence of chlorinated products on the anode surface, the proportion of oil should be sufficient to cover only the inner surface of each pore. In 1925 the use of paraffin, linseed oil, chlorinated linseed oil, naphthalene and chlorinated naphthalene was described, and it was emphasized that the degree of reduction in anode wear brought about by the impregnant depends on the quality of the electrolyte, very little improvement being obtained when pure brine is used.[60] Further proposals for impregnation have been made from time to time[61-64] and patents have been obtained for the use of such impregnating agents as polydivinylacetylene,[65] chlorinated fatty acids,[66] and electrolytically chlorinated linseed oil.[67] A theory of the effect of the impregnant has also been given[68] according to which the impregnant, if properly applied, ensures that electrolysis occurs only at the outer surface of the anode and to a certain depth in the outer pores. In the non-impregnated anode, on the other hand, discharge takes place throughout its entire cross-sectional area and the oxygen content of the anodic chlorine is higher from the pores than from the outside surface, which accounts for the higher rate of destruction of the non-impregnated anode. It is pointed out, however, that if the impregnation is not carefully done the current density and the potential rise to the point where intermediate oxides of graphite are formed which cause a rapid destruction of the anode. In view of this, it is not surprising that there appears to be no generally accepted figure for the increase in anode life brought about by impregnation and that impregnated graphite is not in general use, although it has been reckoned[9] that about one half of American chlorine is made in cells using impregnated anodes. The impregnation is carried out by the graphite manufacturer, using proprietary methods. The question of impregnation is further discussed later with reference to mercury cells (see page 307).

Cathodes

As cathode material, iron or steel appears to be in general use.[8] They have the advantages of cheapness, high strength, good electrical conductivity and high corrosion resistance to the mixture of sodium hydroxide and sodium chloride in the cathode compartment. As to hydrogen overvoltage, no figures appear to have been published giving the results of determinations on a range of metals examined under conditions similar to those which occur in the cathode compartment of the working cell. However, the figures in Table XVII[69] obtained in 1M-sulphuric acid at 25°C. appear to support the choice of iron as cathode material, for this is seen to have a lower overvoltage than the other common metals with the exception of the much more expensive copper. The figures are arranged in order of ascending overvoltage at a current density of 0·1 amp./sq.cm., approximately the value applying in commercial cells.

TABLE XVII. - HYDROGEN OVERVOLTAGES IN VOLTS IN 1M-SULPHURIC ACID AT 25°C.[69]

Material	Current Density in amp./sq.cm.		
	0·01	0·1	1
Platinum Black	0·03	0·04	0·05
Platinum	0·07	0·29	0·68
Gold	0·39	0·59	0·80
Copper	0·58	0·80	1·25
Iron	0·56	0·82	1·29
Carbon	0·70	0·89	1·17
Silver	0·76	0·98	1·10
Aluminium	0·83	1·00	1·29
Mercury	0·93	1·03	1·07
Nickel	0·74	1·05	1·24
Zinc	0·75	1·06	1·23
Lead	1·09	1·18	1·26
Cadmium	1·13	1·22	1·25

No work appears to have been done on the testing of alloys as cathode materials having lower hydrogen overvoltages than iron or mild steel, other than that recently reported where cathode potentials were determined on iron, tungsten and a tungsten-nickel alloy.[70] The measurements were made at 25°C. and at 70°C., at current densities of 0·001 - 0·2 amp./sq.cm. in a solution containing 160 g./l. NaCl and 120 g./l. NaOH and thus resembling the normal catholyte. The potentials on iron and tungsten were similar but on the tungsten-nickel alloy at 70°C. values lower by 0·13 - 0·33 V. were observed, the difference increasing with current density. There is thus some indication from this work that alloys with lower hydrogen overvoltages may be developed for use as cathodes for diaphragm cells, but obviously their cost has yet to be taken into account.

The Diaphragm

It is shown above that the main loss in current efficiency, around 5% in practice, arises from diffusion of hydroxyl ion from the catholyte through the diaphragm into the anode compartment. It is therefore clear that it is important so to design the diaphragm that this loss is as low as is compatible with adequate brine flow from the anode to cathode compartments at low pressure drop, and with low electrical resistance offered by the diaphragm. A further factor that has to be taken into account is that if the diaphragm holes are very small, they tend to block up very quickly with the residual impurities not removed during brine purification so that diaphragm changing becomes unduly frequent. In commercial cells a compromise is accordingly reached in which the type of diaphragm chosen is that giving minimum total operating cost.

A great deal of work has been done on diaphragm design and the patent literature is extensive.

Many different materials such as quartz, corundum, cellulose,[71] polyvinyl chloride,[72] or even alkali chloride have been proposed for use in a cell in which both anolyte and catholyte are kept saturated with chloride,[73] but the diaphragm material in common use is asbestos paper or deposited asbestos fibre either alone or mixed with such materials as barium sulphate.[8,74,75]

At a current density of 0·08 amp./sq.cm. and at 75°C., approximately the conditions found in practice, the resistance of the diaphragm has been given as 0·12 - 0·15 V.,[8] and this potential drop together with a current efficiency loss of about 5% may presumably be taken as representing the best performance attainable in present practice.

The Cell Products

These are hydrogen, chlorine and a sodium hydroxide-sodium chloride solution. A brief account is now given of the procedure by which each of these is purified and made available for commerce.

Hydrogen

The cell gas, after passing through condensing traps[76] to remove most of its water content, and drying by sulphuric acid,[77] appears to be sufficiently pure for most purposes although no detailed analysis of the gas appears to have been published. The hydrogen may be burned with chlorine to give synthetic hydrochloric acid[77] or combined with nitrogen to give synthetic ammonia.[2] It is also used for the reduction of molybdenum and tungsten, for heating in the processing of manganese and chromium ores, for the production of high purity sodium sulphide from sodium sulphate, and for cylinder filling.[78]

Chlorine

In addition to the oxygen and carbon dioxide already shown to be present, the cell chlorine contains water vapour in equilibrium with it, adventitious air, traces of hydrogen which have diffused through the diaphragm, and small concentrations of anolyte spray. Moreover it may contain traces of chlorinated organic matter derived from the impregnant in the anodes and anode connexions or from materials used for sealing the cell or pipelines, as well as bromine from any bromide present in the feed brine. As in the case of the hydrogen, most of the water vapour is separated by simple cooling of the cell chlorine e.g. to 15°C.[12] in direct-contact water scrubbers, or in ceramic or glass pipes through which cooling water is circulated;[8] most of the brine mist is also removed at this stage. The gas is next dried by countercurrent flow of sulphuric acid, e.g. in ceramic and cast iron towers packed with Raschig rings.[12] The acid is used until its strength falls to 50 - 60% H_2SO_4 when it has to be reconcentrated in a sulphuric acid plant.[18] The amount of sulphuric acid used in the drying process depends on the temperature to which the gas was reduced in the initial water-cooling and is of the order of 25 lb. per ton of chlorine.[8] After this stage the gas contains about 0·1 mg. of water per litre[18] and it is then filtered to remove sodium sulphate derived from the action of the sulphuric acid on the sodium chloride in the brine spray originally present in the gas.[79] The concentration of the remaining impurities is then reduced by liquefaction of the chlorine.

The boiling point of chlorine is -34·6°C. and at 30°C. it has a vapour pressure of 8·6 atmospheres. The gas can therefore readily be liquefied by moderate compression, by refrigeration, or by a combination of these processes. A considerable amount of attention has been given to the problem of liquefaction by compression alone[80-84] but so far the only lubricant found which has the required resistance to corrosion by the chlorine heated by the compression is sulphuric acid, which is employed both in reciprocating[79] and in rotary[8] pumps. Considerable maintenance troubles with the reciprocating compressors at the higher pressures[79] and the low mechanical efficiency of the rotary compressor[8] have meant that some degree of refrigeration has been found desirable.[79] Thus in some modern plants refrigeration by Freon (see pages 142,210) has been used on chlorine compressed to 2 – 3 atmospheres[12,13,85] and refrigeration with compression is also employed at the new U.S. Government plant at Muscle Shoals, Alabama.[86] The liquid chlorine is drained from the condenser into storage tanks. The carbon dioxide, oxygen, hydrogen and air are not condensed and are purged from the system with the chlorine gas in equilibrium with the liquid chlorine under the conditions of liquefaction; this weak chlorine purge gas may be utilised for the production of synthetic hydrochloric acid[12] or of sodium hypochlorite solutions.[78,79] In carrying out the liquefaction, care has to be taken that the proportion of the total chlorine liquefied is not so great as to raise the hydrogen content of the purge gas beyond the safe limit, variously given as 5%,[87] 5·5%,[88] 6%[89,90] and normally taken as 6 – 7%.[8] The proportion of a factory output of chlorine which is liquefied depends on whether an outlet for gaseous chlorine is available, e.g. for hydrochloric acid or sodium hypochlorite production, within the factory itself or in the immediate neighbourhood. The total energy consumed in the liquefaction process is about 150 kw.hr. per British ton of chlorine.[2] From the storage tanks, the liquid chlorine is sent into commerce in pressure-tested steel cylinders, drums or rail tanks of a wide variety of sizes[91] and in tank ships.[92] Precautions in the handling of liquid chlorine have been described.[93-97]

Liquid chlorine prepared in this way is substantially free from all the original impurities present in the cell chlorine with the exception of relatively involatile substances like bromine and chlorinated hydrocarbons, and appears to be of sufficiently high purity for use in commerce without further treatment. Where commercial chlorine of special quality has been required this has been obtained by simple distillation of ordinary liquid chlorine.[79] Very little information (see page 270) is available on the impurities present in commercial liquid chlorine and there appears to be no generally accepted specification of quality. The impurities present must depend on the quality of the feed brine, the type of cell used, and the properties of any materials used for impregnation and cell sealing, and it seems clear that if very pure chlorine is needed for any purpose, commercial chlorine should be treated by a process such as distillation which will remove both more volatile and less volatile impurities.

Sodium Hydroxide

The third cell product is a solution containing about 11% by weight of sodium hydroxide and 14 – 15% of sodium chloride, with a small concentration of sodium chlorate of the order of 0·02%. Full descriptions are available of modern practice in the treatment of this product to give a concentrated sodium hydroxide solution and solid salt for re-use in the electrolysis plant.[2,12,98] This is done by concentrating the catholyte in steel and copper evaporators until a concentration of 50% by weight of sodium hydroxide is reached. Salt separates out at each stage of the evaporation as is shown in Table XVIII taken from a report on the operation of the former I.G. plant at Rheinfelden.[98]

TABLE XVIII.- EVAPORATION OF DIAPHRAGM CELL CATHOLYTE: COMPOSITION OF SOLUTION AT VARIOUS STAGES[98]

	g./litre	
	Sodium Hydroxide	Sodium Chloride
Fresh Catholyte	120	175
Stage 1	278	160
Stage 2	290	130
Stage 3	335	80
Stage 4	750	44
Sodium Hydroxide for sale	760	15

Sodium hydroxide solution prepared in this way and containing about 50% by weight of sodium hydroxide and 1% of sodium chloride is suitable for many purposes but its chloride and chlorate contents make it unfit for making rayon.[2,98] The crude solution may, however, be purified in several different ways:-[2,98]

(1) by cooling so as to separate one of the hydrates of sodium hydroxide such as $NaOH,2H_2O$, $NaOH,3{\cdot}5H_2O$, or $NaOH,7H_2O$ followed by centrifuging and, if necessary, re-evaporation;

(2) by dialysis followed by re-evaporation;

(3) by extraction of the chloride and chlorate with liquid ammonia.

Typical analyses of the ordinary quality and of the purified sodium hydroxide solutions are given in Table XIX.[2]

TABLE XIX.- ANALYSES OF DIAPHRAGM CELL SODIUM HYDROXIDE SOLUTION[2]

	Concentration in weight per cent. in	
Substance	Ordinary Quality Solution	Purified Solution
NaOH	50·00	50·20
Na_2CO_3	0·1–0·3	0·3
NaCl	1·00	0·16
$NaClO_3$	0·05–0·10	0·0004
Fe	0·0005	0·0005
Cu	0·00003	0·00004

Sodium hydroxide is supplied both as solution of 40–50% concentration and in the solid state.[99] The solution is shipped in steel drums, road and rail tanks of various sizes, and occasionally[100] in special tank ships. When it is desired to keep the solution as pure as possible, it may be transported in Neoprene-lined containers.[101] When solid is required, this solution is evaporated to 70% sodium hydroxide content[98] and is then 'finished' in cast iron pots heated either by direct firing with coal[99] or gas,[98] by electricity[102] or by a heat exchange medium such as diphenyl.[99,103,104] Processes have been devised whereby an immiscible diluent such as paraffin[99,105] or diphenyl[99] is added to the 50% sodium hydroxide liquor, and the water content is removed, together with the diluent, by distillation. A typical analysis of the finished solid caustic soda is given in Table XX.[98]

The solid is packed in the molten state into thin sheet steel drums for shipment.[99]

TABLE XX. - ANALYSIS OF SOLID SODIUM HYDROXIDE FROM DIAPHRAGM CELL PROCESS[96]

Constituent	%
NaOH	96·9
Na_2CO_3	0·8
Na_2SiO_3	0·1
NaCl	2·1
$NaClO_3$	Nil
Na_2SO_4	0·06
Fe_2O_3	0·006
Al_2O_3	0·005
BaO	0·0037
MgO	0·0009

THE ELECTROLYSIS OF BRINE IN MERCURY CELLS

A very short account of this process, illustrated by the Castner 1893 cell, was given in the original Treatise (Mellor,II,36). The process has remained basically the same but, as in the case of diaphragm cells, there has been a marked tendency for cell capacity to increase as development has proceeded. Thus the original cells installed at the end of last century had a capacity of about 500 amp.;[106] a circuit of 54 such cells was installed in 1897 at Saltville, Va. and, mechanically improved in several ways, is still producing chlorine.[31] By 1920 the size had increased to 4000 amp.[107] while in 1932 a description was given of cells with a capacity of 9000 amp.[108] In 1951 cells using 30,000 amp. were in routine operation.[109] This great increase in capacity means that cells are now in use each of which would produce almost one ton of chlorine per day.

Main Features of Modern Cells

In the last decade a considerable amount of information has been published on the operation of modern mercury cells. Thus full constructional details are available on the types and operation of cells in use in Germany during the 1939-45 war.[20,77,78,110-113] In addition, post-war developments in U.S.A. have been described.[13,31,87,109,114,115] The detailed information published on the new Mathieson cells[31,87,115,116] in operation in U.S.A. has been used in drawing Fig. 2, and in the following description of the main features of a modern cell. The cell illustrated is of 30,000 amp. capacity. Fig. 2(*a*) shows a transverse view of the cell and Fig. 2(*b*) a longitudinal view.

The cell consists of two main parts, the electrolyser or brine cell and the decomposer or denuder. The brine cell is essentially a closed rectangular trough, very long in comparison with its height and breadth, and sloping along its length. The base of the cell is a single sheet of steel set on insulated feet (not shown). The sides are of rubber-covered steel bolted to the base plate and sealed with soft-rubber gaskets. The cover is a single piece of steel, reinforced to prevent flexure, and rubber-covered on all parts liable to be exposed to attack by wet chlorine and chlorinated brine. The inlet and outlet compartments, which close the ends of the cell and house the brine inlet, chlorine outlet and brine outlet, are of rubber-lined cast iron. The outlet compartment is fitted with a removable cover for cell inspection. The graphite anodes, which have saw cuts on their under surfaces to facilitate the removal of the chlorine gas liberated there, lie almost horizontally a short distance above the base plate, and current is led to them through brass pipes which are protected from corrosion by porcelain sleeves. The upper parts of the metal pipes are threaded, to permit adjustment of the height of the anodes above the mercury layer which acts as the cathode, and the lower parts are

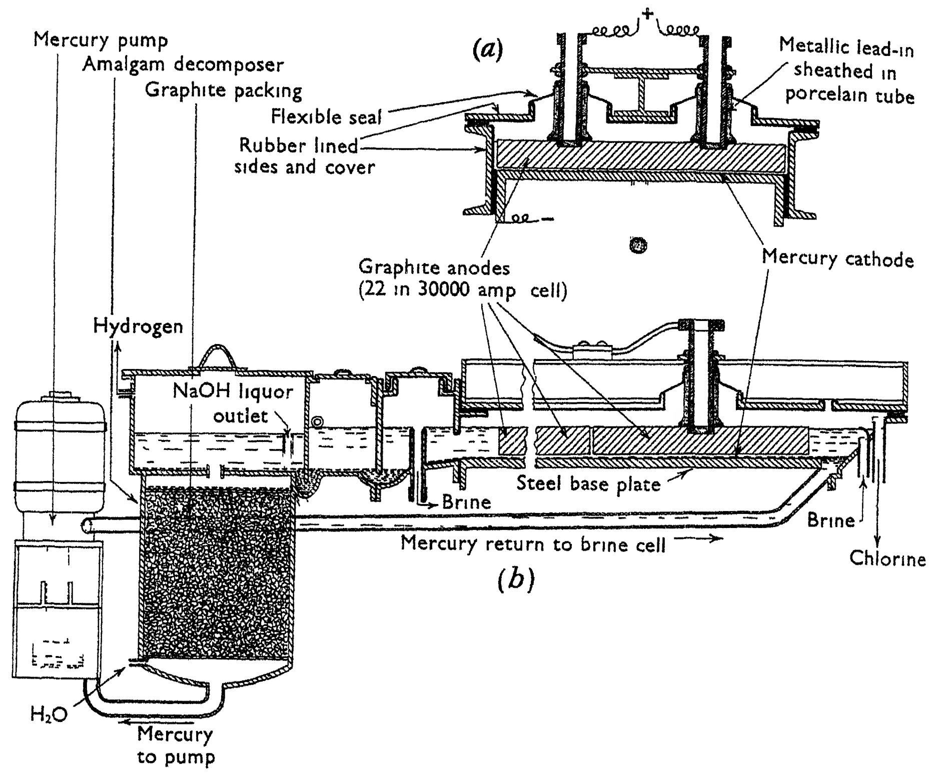

(a)
+
Mercury pump
Amalgam decomposer
Graphite packing
Flexible seal
Rubber lined sides and cover
Metallic lead-in sheathed in porcelain tube
Graphite anodes (22 in 30000 amp cell)
Mercury cathode
Hydrogen
NaOH liquor outlet
Steel base plate
Brine
Brine
Chlorine
Mercury return to brine cell
(b)
H₂O
Mercury to pump

Fig. 2. MATHIESON E-8 MERCURY CELL

attached to lead buttons which are threaded and then screwed into holes in the anodes as shown. The graphite round each of these holes is impregnated to prevent corrosion by the chlorinated brine which otherwise would penetrate to the threaded lead buttons. There are two of these current connections to each anode block, and flexible seals as shown in Fig. 2 permit the anode assembly to be moved up and down without escape of chlorine from the gas space in the cell. Anode and cathode connexions are fitted above and below the brine cell respectively.

The denuder consists of a cylindrical steel tower, flanged at its upper end, and having a domed lower end. In the lower part of the tower pieces of graphite are held between screens. The upper part of the tower is fitted with an amalgam inlet, and with exits for sodium hydroxide solution and hydrogen, while the lower part contains a water inlet and an outlet through which mercury passes to a sump. An electrically driven centrifugal pump draws mercury from this sump and discharges it into the electrolyser at its inlet end; a signal light is fitted, to give warning if the pump motor fails.

In addition to the above horizontal brine cell, which is the type most used to-day,[2] vertical brine cells were designed and operated in Germany before and during the 1939-45 war in order to obtain maximum chlorine output from a given floor space.[117-120] Here the mercury pump and the decomposer were of the type described above but the electrolyser had some novel features. Four or five vertical steel discs, about 1·8 m. in diameter and separated from each other by a distance of 11 – 20 cm., rotate at about 7 r.p.m. and dip into a semi-cylindrical steel basin containing amalgam; the surface of the discs above the amalgam reservoir thus become coated with amalgam and can then be made cathodic. The graphite anodes are set vertically opposite and as near as possible to both sides of the discs, above the amalgam reservoir. The upper part of the cell encloses the anodes and cathode discs, and contains the brine to be electrolyzed; it is made of rubber-lined steel and is run almost full of brine. The chlorine is taken off above the brine level and the amalgam leaves the cell at the side where it meets the discs travelling downward. The brine and amalgam concentrations are similar to those found in the horizontal cell described above. One complete cell occupies about 5·5 sq.m. of floor area and has a capacity of 24,000 amp. at a cathode current density of 0·17 – 0·24 amp./sq.cm., depending on the exact type of vertical cell used. However, cell voltages are high because of the difficulty in adjusting the anode-cathode gap, and the hydrogen content of the chlorine is higher than with horizontal cells because of the discharge of the amalgam produced by pieces of graphite, which fall from the anodes and cannot readily be removed from the surface of the amalgam reservoir. As a result of these and other drawbacks, chlorine produced in vertical cells costs about 50% more than that made in horizontal cells. There is no reference in the literature to any extension of the use of vertical cells in Germany in post-war years, or to their adoption in any other country, and they need not be further discussed here.

Operation

The mercury circulation is first started and then brine at about 60°C., purified as described above and containing about 26% of sodium chloride, is fed to the electrolyser and water is fed to the denuder. The current is then switched on.[87] Reaction I, below, then occurs in the brine cell, and reaction II in the denuder:-

$$NaCl_{soln.} + Hg \rightarrow NaHg + \tfrac{1}{2}Cl_2 \ldots\ldots\ldots\ldots \text{I}$$

$$NaHg + H_2O \rightarrow NaOH + \tfrac{1}{2}H_2 + Hg \ldots\ldots\ldots\ldots \text{II}$$

where NaHg represents a dilute sodium amalgam. It should be noted that in reaction I only a fraction of the total brine entering the cell is electrolyzed in practice, and that in reaction II the amount of water actually used is that necessary to decompose the amalgam and form a sodium hydroxide solution of the concentration required.

The chlorine formed at the anode leaves the cell saturated with water vapour at the prevailing brine concentration and cell temperature. In addition, it contains a small amount of hydrogen, normally of the order of 1% by volume of the chlorine, formed by discharge of hydrogen ion at the amalgam surface

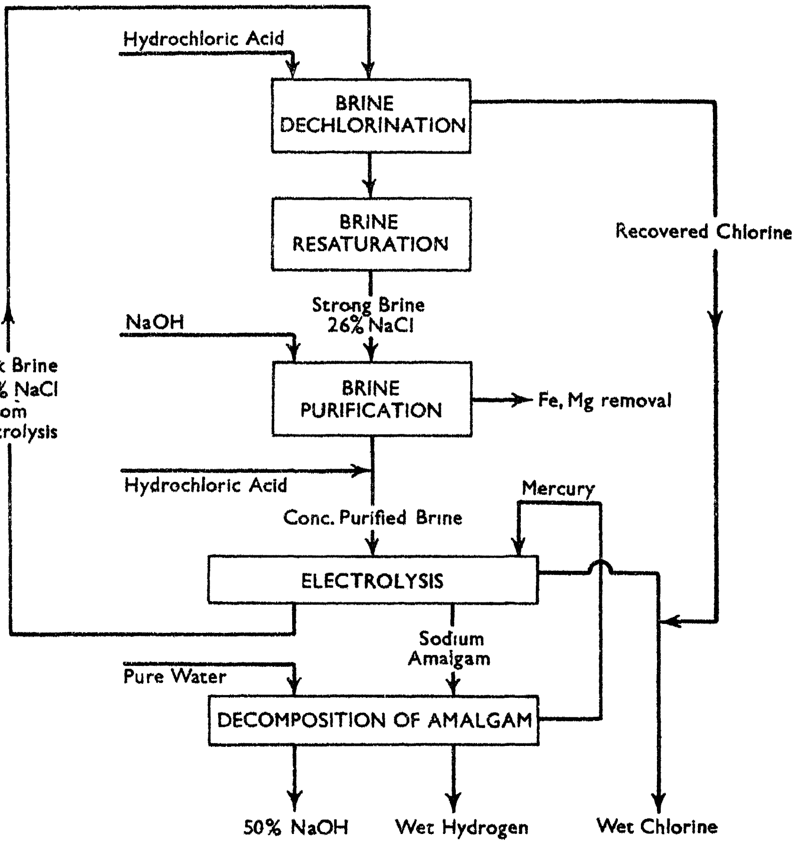
$$H^+ + e \rightarrow \tfrac{1}{2}H_2 \ldots\ldots\ldots\ldots \text{III}$$

The rate of circulation of the mercury is adjusted so that the sodium content of the amalgam leaving the brine cell is 0·1 – 0·2% by weight. The amount of water used in the denuder is normally that required to give a solution containing about 50% by weight of sodium hydroxide. The hydrogen produced in the decomposer leaves the system saturated with water vapour at the prevailing temperature and concentration of the sodium hydroxide with which it is in contact;[87] the hydrogen also contains traces of mercury vapour.[2]

The brine is fed to the cell at such a rate that the sodium chloride concentration in the exit brine is about 23·5%.[87] The exit brine, containing small proportions of hypochlorous acid and chlorate formed in the cell, is treated with the small amount of hydrochloric acid needed to convert these into chlorine, which is then removed from the hot brine and recovered by extraction under vacuum followed by air-blowing,[87,112] or by air-blowing alone.[13]

The dechlorinated brine is next resaturated by passing through fresh solid salt and is again purified (see page 275), in order to remove impurities, especially iron and magnesium, which have a harmful effect on cell performance. The magnesium, as well as calcium and sulphate, is present in the solid salt, while iron or other elements may be introduced in minute concentrations from the graphite anodes during the electrolysis.[121] Purified brine, slightly acidified by hydrochloric acid, is thus again available with a sodium chloride concentration of about 26%.

The main features in the operation of a mercury cell plant may be summarized thus:-


Hydrochloric Acid
BRINE DECHLORINATION
BRINE RESATURATION
Recovered Chlorine
Strong Brine 26% NaCl
NaOH
Weak Brine 23·5% NaCl from Electrolysis
BRINE PURIFICATION
Fe, Mg removal
Hydrochloric Acid
Mercury
Conc. Purified Brine
ELECTROLYSIS
Sodium Amalgam
Pure Water
DECOMPOSITION OF AMALGAM
50% NaOH
Wet Hydrogen
Wet Chlorine

Further consideration will now be given to the various aspects of the operation of the electrolyser and denuder, and to the treatment of the three cell products, chlorine, hydrogen and sodium hydroxide. The purification of the brine has already been dealt with (see page 274) and will be mentioned again only in relation to the effect of impurities in the brine on cell operation.

Energy Consumption in the Cell

The electrical energy in kilowatt-hours consumed in the production of one ton of chlorine, $E = 76{,}810 \frac{V}{C}$ where V is the cell voltage and C the percentage current efficiency, follows from a simple application of Faraday's laws.

With modern cells, the voltage is that determined for the brine cell because, unlike earlier cells, these have no provision for attempting to recover electrical energy from the operation of the denuder, this apparently having been abandoned as uneconomical.[122] In computing the energy efficiency below, however, it is assumed that the denuder should theoretically be able to yield electrical energy and, therefore, the practical figure for energy efficiency is obtained by dividing the energy theoretically required to produce sodium hydroxide and chlorine from the brine, *i.e.* the reference figure 1682 kw.hr. (see page 278), by the electrical energy actually consumed in the operation of the electrolyser. The minimum energy requirement obviously results when the electrolysis is done at the reversible voltage and when 100% current efficiency is obtained, *i.e.* in the complete absence of any cell reaction other than (I) above. Figures of +1·334V. and -1·738V. have been given for the reversible anode and cathode potentials at 65°C. with 25·5% sodium chloride in the brine and 0·02% by weight of sodium in the amalgam.[123] Other values may be deduced from results recently published, by extrapolating to zero current density figures for the variation of anode and cathode potentials over a range of current densities.[114] The figures obtained in this way for the anode and cathode potentials at zero current density are +1·33 and -1·70V., giving a reversible voltage of 3·03 which applies to the following average conditions under which these experiments were done:- brine concentration 24·7% NaCl, sodium concentration of amalgam 0·05% by weight, temperature 67·5°C. These are near the conditions under which modern cells work, as shown above, and so 3·03V. may be used as an approximate value for the reversible voltage under practical cell conditions. With this value for V in the above equation it follows that, at 100% current efficiency, the theoretical energy requirement is 2327 kw.hr. per ton of chlorine.

The figures in Table XXI have been published for the energy consumption at different current densities on a 15,000 amp. Mathieson cell similar to the type described above.[115] The energy efficiencies in the Table have been calculated from the reported energy consumption figures and the theoretical value, 2327 kw.hr.

TABLE XXI. - ENERGY CONSUMPTION IN THE MERCURY CELL PROCESS

	Data for Mathieson Cell		
Cell Current: amperes	6,250	12,500	15,000
Anode Current Density amp./sq.cm.	0·1	0·2	0·24
Chlorine per cell per day: tons*	0·180	0·377	0·452
Average Cell Voltage	3·73	4·11	4·25
Current Efficiency: %	95	95	95
Energy Consumption: kw.hr./ton of chlorine*	3,001	3,326	3,472
Energy Efficiency: %	56·0	50·6	48·4

* These are the published figures converted to British tons; the figures for chlorine output and energy consumption derived from the other results in the Table are slightly different.

A somewhat higher figure, 3678 kw.hr. per ton of chlorine, giving an energy efficiency of 45·7%, is reported for German cells of 5 sq.m. cathode area using 13,400 amp. at a cathode current density of 0·268 amp./sq.cm.[2] The reasons for the loss in energy efficiency are discussed below (see also page 299).

Voltage

It has been shown that under normal working conditions the cell voltage is around 4V., depending on the current density being used. This voltage is considerably higher than the approximate reversible voltage, 3·03V. The reasons for the difference are similar to those already given in the section on diaphragm cells and are as follows:-

(*a*) there is a high overvoltage of chlorine at the anode and a small overvoltage of sodium at the cathode;

(*b*) there are potential drops through the electrolyte gap, through the anode and cathode leads, and through the various contacts.

A detailed account is given in a recent paper of the contribution made by each of these factors in a modern de Nora mercury cell, the principles of which are similar to those of the Mathieson cell described above.[114] The feed brine used in the experiments had the following average composition:- sodium chloride 305 g./l., sodium sulphate 2 – 4 g./l., sodium chlorate 1 – 2 g./l. and calcium sulphate 0·05 – 0·5 g./l. In the earlier experiments the brine contained 0·01 – 0·1 g./l. of sodium hydroxide and 0·01 – 0·2 g./l. of sodium carbonate, but later the cells were fed with acid brine containing 0·01 g./l. of hydrochloric acid. The exit brine from the cell contained 275 g./l. of sodium chloride and thus the average concentration was 290 g./l. The average cell temperature was 67·5°C. and the average concentration of sodium in the amalgam was 0·05% by weight. The graphite used as anode was of British Acheson type X and it had been in use for 6 weeks before the anode potentials given in Table XXII were determined.

It is pointed out that it was not possible to obtain very accurate results for the anode and cathode potentials or for the potential drop in the electrolyte since a change in position of the tip of the calomel electrode used in the measurements by as little as 0·8 mm. caused a variation of 30 – 40 millivolts in the reading.

TABLE XXII. - VOLTAGE DISTRIBUTION IN A DE NORA MERCURY CELL[114]

Potential (negative) in volts

Current: amperes	6,000	9,000	12,000	15,000	18,000
Anode Current Density: amp./sq.cm.	0·123	0·184	0·245	0·306	0·368
Cathode Current Density: amp./sq.cm.	0·105	0·158	0·210	0·263	0·315
Anode Potential	1·500	1·580	1·660	1·740	1·830
Cathode potential	1·740	1·760	1·780	1·800	1·820
Potential Drop in 4·8 mm. electrolyte	0·110	0·180	0·240	0·300	0·370
Potential Drop in Conductors[1]	0·098	0·143	0·188	0·231	0·274
Potential Drop in Contacts[2]	0·036	0·064	0·070	0·088	0·106
Cell Voltage	3·484	3·727	3·938	4·159	4·400

Note:

1 includes inter-connecting bus bars, anode equalising bar, branch band, anode collar, graphite rod, graphite anode plate, mercury cathode, cathode plate – cathode bar.

2 includes bus bar/anode, copper equalising bar/branch band, branch band/anode collar, anode collar/graphite rod, graphite rod/graphite plate, mercury/steel plate and cathode bar–bus bar.

The approximate reversible chlorine potential under cell conditions obtained by plotting the anode potentials to zero current density is +1·33V., and this indicates that the chlorine overvoltages reached the high figure of 0·5V. at 0·368 amp./sq.cm., the highest current density for which results are given. At the lowest current density, 0·123 amp./sq.cm., the anode potential, 1·50V., is in good agreement with Stender's results given in Table X (page 278).

The cathode potential extrapolated to zero current density is –1·70V., and the over-potentials thus range from 0·04 to 0·120V. at the current densities studied. These over-potentials are much lower than those applying at the anode, in agreement with the fact that the highest values for over-potential are obtained when gases are liberated at an electrode. The cathode potentials determined in this work are about 0·1V. lower than those given in earlier work,[124] but are close to those reported in some German work.[125] They are also close to results given in 1953 by Russian workers who determined amalgam potentials at different current densities, temperatures and sodium concentrations.[126] This work was done on a laboratory scale, and a stirred cathode was used which was separated from the anode by means of a diaphragm made of sintered glass. Those results which are most relevant to mercury cell operation are summarized in Table XXIII.

TABLE XXIII.- VARIATION OF SODIUM AMALGAM POTENTIAL WITH CURRENT DENSITY AND SODIUM CONCENTRATION[126]

Sodium Chloride Concentration 300 g./l.: Temperature 65°C.					
Sodium in Amalgam, Percent by Weight	Current Density amp./sq.cm.				
	0·05	0·09	0·12	0·20	0·30
	Potential in Volts				
0·05	$1{\cdot}76_0$	$1{\cdot}76_6$	$1{\cdot}77_2$	$1{\cdot}77_6$	$1{\cdot}78_0$
0·10	$1{\cdot}77_2$	$1{\cdot}78_4$	$1{\cdot}77_8$	$1{\cdot}79_2$	$1{\cdot}79_6$
0·15	$1{\cdot}79_0$	$1{\cdot}79_8$	$1{\cdot}80_1$	$1{\cdot}80_6$	$1{\cdot}81_0$
0·20	$1{\cdot}80_0$	$1{\cdot}80_8$	$1{\cdot}81_3$	$1{\cdot}81_8$	$1{\cdot}82_2$
0·25	$1{\cdot}81_1$	$1{\cdot}81_6$	$1{\cdot}82_4$	$1{\cdot}82_8$	$1{\cdot}83_6$
0·30	$1{\cdot}82_0$	$1{\cdot}82_8$	$1{\cdot}83_4$	$1{\cdot}84_0$	$1{\cdot}85_1$
0·33	$1{\cdot}82_6$	$1{\cdot}83_4$	$1{\cdot}84_1$	$1{\cdot}84_4$	$1{\cdot}85_7$

The values for the potential drops through 4·8 mm. of electrolyte are close to those derivable from the figures in Table XIII and suggest that the resistance resulting from the chlorine gas bubbles liberated on the underside of the anodes is not included under this head. It thus seems probable that the gas bubble resistance, not specifically allowed for in Table XXII, is included in the figures for anode potential.

The figures in Table XXII thus readily explain the divergence between the theoretical and working voltages in a mercury cell and explain the directions in which savings in voltage have been attempted. Thus the resistance arising from the gas bubbles is an important factor, as shown by the attention given in modern cells to slotting and drilling of the anodes to facilitate gas release.[18,31,115] Again, a claim has been made that a decrease in voltage is achievable by adding to the brine 0·001 – 0·02% of a substance which exerts a wetting action at the graphite surface, and in this way reduces the chlorine gas film resistance.[127] The important amount of energy lost through resistance of the electrolyte emphasizes the need to keep to a minimum the electrolyte gap between anode and cathode, and in modern cells this is achieved by frequent movement of the anode to compensate for anode wear.[31,114,115,128-130] The possibility of reducing chlorine overvoltage at the graphite anode has already been discussed in the section on diaphragm cells. The cathode potential at current densities of 0·1 – 0·3 amp./sq.cm. is reduced by 0·04 – 0·07V. by diminishing the sodium content of the amalgam from 0·2 to 0·02%,[124] but this saving in voltage is gained at the expense of the extra energy required for the more rapid circulation of the amalgam.

Current Efficiency

As in the case of the diaphragm cell, it is customary and convenient to express the current efficiency as the per cent. ratio of the weight of sodium hydroxide produced to that theoretically liberated by the quantity of electricity used, despite the fact that in the mercury cell the cathode product is, strictly speaking, sodium amalgam, which has to react with water in a separate part of the apparatus to give the solution of sodium hydroxide. No information appears to have been published giving both cathode and anode current efficiencies for mercury cells, although it is normally assumed that they are equal.

No detailed current efficiency studies on mercury cells have been made of the kind published for diaphragm cells,[33] and so the reason for the losses in current are much less clear. These losses amount to 4 – 10%.[2,108,115,131] As with the diaphragm cell, there may be leakages of current to earth, or current may pass from anode to cathode non-electrolytically. For reasons similar to those given for diaphragm cells, this loss is probably small. Since mercury cell sodium hydroxide is more easily processed than the mixture of sodium hydroxide and sodium chloride made in the diaphragm cell, it may be assumed that losses in the working up of the mercury cell products will be smaller than in the case of diaphragm cells. This leaves three main sources of current loss; that resulting from the discharge of hydroxyl ion instead of chlorine at the anode, that arising from the discharge of hydrogen ion instead of sodium ion, giving hydrogen in the cell chlorine, and that arising from cathodic reduction of chlorine dissolved in the brine. These are now dealt with in turn.

The Discharge of Hydroxyl Ion at the Anode

Hydroxyl ion as well as chloride ion is discharged at the graphite anode, and the general theory, discussed above for diaphragm cells (see page 281), applies here with the difference that the pH of the brine in the mercury cell is probably about 2 (see next page), while in the anolyte of the diaphragm cell it is about 4. The proportion of carbon dioxide by volume in the chlorine from mercury cells depends on cell conditions, and figures of 0·3 – 1·5% have been given.[10,112,115] This involves a loss of anodic current efficiency of 0·6 – 3·0% since the reaction involved is held to be

$$4OH^- + C \rightarrow CO_2 + 2\,H_2O + 4e$$

as compared with the main anode reaction

$$2Cl^- \rightarrow Cl_2 + 2e.$$

The effect of various factors on the amount of hydroxyl ion discharged is dealt with later (see page 306).

The Discharge of Hydrogen at the Cathode

As pointed out above, the reaction $H^+ + e \rightarrow \frac{1}{2}\,H_2$ takes place to a small extent in the brine cell. This hydrogen is carried from the cell in the chlorine, where it is found in the proportion of about 1% by volume.[10,18,115] This means a loss of current efficiency of about 1%.

Theory

At first examination, it is surprising that the extent of hydrogen ion discharge should be so small, since the electrode potential of sodium is so much more negative than that of hydrogen. In solutions of unit molality of hydrogen ion and of sodium ion at 25°C., these standard potentials are respectively 0 and −2·71V. The conditions in the working cell are, however, quite different and the following factors have to be taken into account:-

(*a*) the sodium ion concentration in the electrolyte is high and that of hydrogen ion is low;

(*b*) sodium is soluble in the mercury cathode and compound formation occurs;

(*c*) the hydrogen overvoltage at a mercury cathode is very high;

(*d*) the hydrogen ion concentrations near the cathode surface may possibly be extremely low.

In practice, a concentrated sodium chloride solution, about 5 molal, is electrolyzed, the hydrogen ion concentration of the solution being controlled by the chlorine hydrolysis reaction discussed with reference to diaphragm cells (see page 283). No figures appear to have been published on the pH of the brine in mercury cells, but an estimate may be made from the results given in Table XV on the pH of the anolyte in a diaphragm cell. The results for run 23 may be taken as indicating that the brine in mercury cells has a pH of about 2, since in this run the anolyte sodium chloride concentration was close to that of the brine in mercury cells, and the amount of alkali entering the anolyte was somewhat smaller than that liberated in mercury cell brine by hydrogen discharge at the cathode and equivalent to the normal 1% of hydrogen in the cell gas.

The solubility of sodium in mercury with compound formation results in sodium discharge potentials which, as shown above, are only about -1·8V. in a working cell at a current density of about 0·2 amp./sq.cm. Measurements have been made of the variation of potential with current density for the discharge of sodium and potassium ions from concentrated aqueous solutions of their chlorides and hydroxides. The polarization potential, π, was related to the current density D^1 by the expression $\frac{D^1}{\pi} = -0{\cdot}058 \log (1 + \frac{D^1}{K_1})$, where K_1 is proportional to the initial concentration of the amalgam and the rate of flow of the mercury. It was considered that polarization is not caused by delayed discharge or by oversaturation but probably arises through delayed diffusion of sodium or potassium into the mercury. Results from a stationary mercury cathode, with constant stirring of the solution, confirm these conclusions and show that K_1 does not depend on the solvent used.[132]

On hydrogen overvoltage in mercury, determinations have recently been made under some of the conditions which apply in practice. It has been shown that the constants of the Tafel equation, $\eta = a - b \log i$, on mercury, in hydrochloric acid solution of concentrations between 0·01N. and N., are $a = -1{\cdot}395$ and $b = 0{\cdot}113$ for the current density range $10^{-6} - 10^{-1\cdot5}$ amp./sq.cm., and that the temperature coefficient of overvoltage is about -0·003V./°C. rise in temperature.[133] When a commercial cell is working at a cathode current density of 0·2 amp./sq.cm. the current density applying to hydrogen ion discharge is only about 1% of this, since in practice this is the proportion of the current which causes hydrogen formation. On this basis the hydrogen overvoltage on mercury in a working cell in brine at 20° is -1·09V. at 70°C.; the value on the above temperature allowance would be approximately -0·94V. Since the hydrogen potential is zero at unit hydrogen ion concentration, this means that the actual hydrogen discharge potential at the mercury surface is -0·94V. at unit hydrogen ion concentration. In experiments with the dropping mercury cathode, it has been shown that the dependence of the discharge potential of hydrogen ion in acid solutions on the concentration of hydrogen ion is given by

$$\pi_1 - \pi_2 = \frac{2RT}{F} \ln \frac{C_1}{C_2}$$

where π_1 and π_2 are the potentials, C_1 and C_2 the hydrogen ion concentrations, and where R, T and F have their usual meaning.[134] Hence at pH 2 and at 70°C. the hydrogen discharge potential is -0·94 - 0·28 = -1·22V. This is far below the working cathode potential, -1·80V., a potential which, on the basis of the hydrogen overvoltages in mercury, should cause the whole cathode process to be one of hydrogen ion discharge. A suggested explanation of this discrepancy, and of the small proportion of hydrogen ion actually discharged, is that near the amalgam surface the hydrogen ion concentration is much lower than in the bulk of the electrolyte.[122] To cover the difference, -0·58V., between the observed -1·80V. and the calculated -1·22V., there would have to be, on this supposition, a reduction of hydrogen ion concentration to 10^{-4} of that obtaining in the bulk of the electrolyte, *i.e.* the pH of the electrolyte near the amalgam surface would be about 6. A suggestion has been made that the pH of the brine layer near the amalgam is about 9, but no experimental work to determine the value appears to have been done.[123]

Effect of Impurities

While no complete explanation has been given for the very fortunate result that only a small proportion of hydrogen ion is discharged at the cathode under normal working conditions, much information has been collected on the various impurities which influence this proportion.

The reason for the emphasis is that safe working of the brine cell demands that only very small proportions of hydrogen are liberated into the chlorine. This is normally achieved in routine operation but, even in modern plants, dangerously large concentrations of hydrogen sometimes arise because of impurities in the brine. In a recent example of this, the high hydrogen content of the chlorine was traced to impurities present in the graphite anodes.[112,135] It may be noted that, once the hydrogen has been produced, the cell gas may be treated so as to effect combination of the hydrogen with its equivalent of chlorine either by heating,[136-138] or by photochemical means.[139-142] However, this procedure, which was tested in Germany during the last war, has not been reported as being used in the most modern cell plants.

Fifty years ago the harmful influence under certain conditions of magnesium, iron, nickel and cobalt in the feed brine was recognized as well as the fact that calcium, in concentrations up to the limit of its solubility in the brine as calcium sulphate, had little effect on hydrogen discharge.[143] About the same time, the influence of even extremely small concentrations of impurities on the rate of decomposition of sodium amalgam was shown by adding amalgam to two tubes, one containing ordinary distilled water and the other containing water of very high purity. Vigorous liberation of hydrogen occurred in the tube containing the ordinary distilled water but little action took place in the other.[144] Since then, determinations have been made of the influence of many impurities in the brine on discharge of hydrogen at the cathode. The effects of cationic impurities are summarized in Table XXIV. Included in the table are results obtained under laboratory conditions on the decomposition of amalgam in the absence of sodium chloride; it is not known how far the results so obtained apply to working cells, but the variation in several of the results may possibly arise because the method of test was not the same in all cases.[135,145-147]

These effects on amalgam decomposition are sometimes detectable at extremely low concentrations of the impurity. This is borne out in a recent investigation where sodium amalgam was shaken with buffered sodium chloride solutions to which the impurity had been added, and the rate of hydrogen evolution was then determined.[135] Thus the rate of hydrogen production was more than doubled when 0·125 mg. per litre of vanadium was present in the brine. In addition, an important effect known for many years, the promoting action of one impurity on another in bringing about hydrogen formation,[143] has been investigated in more detail.[135,149] Thus it was found that, although 2·5 mg. per litre of iron alone had little effect on the rate of hydrogen production, the addition of only 0·25 mg. per litre of iron more than doubled the rate obtained when 0·125 mg. per litre of vanadium was present. Similar effects were detected with copper and vanadium, arsenic and vanadium and, to a lesser extent, with iron and magnesium. No theories appear to have been advanced to account for these facts, other than the suggestion that the metals which markedly accelerate amalgam decomposition are those which have a very

TABLE XXIV. - INFLUENCE OF CATIONS IN FEED BRINE ON HYDROGEN DISCHARGE AT THE CATHODE IN A MERCURY CELL

Cation	Influence
Aluminium	Very harmful;[148] harmful;[145,146] little effect.[149]
Arsenic	Little effect alone; acts as promoter.[149]
Barium	Harmful;[112] no effect.[135,148]
Calcium	Harmful;[146] doubtful;[112] no effect.[115,135,143,150,151]
Chromium	Very harmful.[112,135]
Cobalt	Harmful;[143] no effect.[146]
Copper	Harmful;[147] slightly harmful;[145] little effect alone, acts as promoter.[149]
Iron	Very harmful;[115] harmful;[112] variable;[148] little effect alone, harmful with Mg;[143] little effect alone, acts as promoter.[135]
Lead	Harmful;[145] no effect.[152]
Magnesium	Harmful;[112,115,148,151] variable;[146] no effect alone; acts as promoter[135] with iron.[143]
Manganese	No effect.[135]
Molybdenum	Very harmful.[112,135]
Nickel	Very harmful;[143] no effect.[135]
Silver	Little effect.[145]
Tantalum	Very harmful.[149]
Titanium	Harmful;[146] fairly harmful.[149]
Tungsten	No effect.[135]
Vanadium	Very harmful.[19,112,118,135,149]
Zinc	No effect.[147]

low solubility in mercury,[147] but the practical outcome of these recent results is an emphasis of the importance of the thorough purification of the brine for use in mercury cells, as shown in a recent patent for the use of a lead salt for the precipitation of anionic vanadium, chromium and molybdenum.[153]

According to a recent patent,[154] control of the pH of the brine in the cell within the range 1·7 – 3·5 minimizes hydrogen ion discharge at the cathode.

Effect of Anions

The effect of various anions on the decomposition rate of sodium amalgam has been examined by shaking amalgam with buffered sodium chloride solution to which the anion has been added, followed by determination of the rate of evolution of hydrogen.[155] It has been shown that bromide and iodide contents up to 0·1 g./l. in the brine have no effect, and that chlorate in a similar concentration has also no influence. Sulphate up to a concentration of 8 g./l. and fluoride in low concentrations are harmless. Nitrate increases the decomposition rate. A very interesting result of this investigation is that anions such as silicate and stannate are able to reduce the harmful influence of such metals as vanadium and molybdenum. Thus the harmful effect of 0·5 mg. per litre of vanadium was completely annulled by the addition of 10 mg. per litre of silicon as sodium silicate, and the influence of 1 mg. per litre of vanadium was annulled by 5 mg. per litre of tin as sodium stannate. Similar but less pronounced effects were obtained with borate and with pyrophosphate. The beneficial effect of these anions is ascribed to their ability to form complexes with the harmful metal. The use of silicate to reduce losses of current efficiency has recently been patented.[156]

Effect of Amalgam Concentration

Under normal conditions the sodium content of the amalgam leaving the electrolyser is 0·1 – 0·2% by weight. If this proportion should increase, e.g.

through incomplete removal of the sodium from the amalgam in the denuder, the hydrogen content of the cell gas may rise above the normal figure of about 1%;[112,115] no figures appear, however, to have been published giving the exact relation between hydrogen content of the cell gas and the sodium content of the amalgam.

Effect of Sodium Chloride Concentration

The hydrogen content of the cell gas increases as the average concentration of sodium chloride in the brine is reduced.[112,115] Table XXV is derived from some recent results.[115]

TABLE XXV.- EFFECT OF SODIUM CHLORIDE CONTENT OF BRINE ON HYDROGEN CONTENT OF CELL CHLORINE. FEED BRINE AT 40°C.

Mean NaCl Content g. per. l.	Cell Voltage	Hydrogen in Chlorine. % by volume
285	4·03	0·23
275	3·97	0·35
265	3·96	0·53
255	3·97	0·73
245	3·99	0·9

Effect of Temperature

This was investigated in Germany in 1938.[157] A range of cell temperatures was obtained by passing the feed brine to a works cell through a heater but, unfortunately, only the brine temperatures are quoted and not the more important cell temperatures. The average sodium chloride concentration of the brine is not stated but from other information[112] was probably about 24·7%. The average sodium content of the amalgam leaving the cell was 0·104% by weight.

TABLE XXVI.- INFLUENCE OF TEMPERATURE ON HYDROGEN CONTENT OF CELL CHLORINE.[157]

Feed Brine Temperature °C.	Voltage	Hydrogen in Chlorine: % by volume
39	4·34	0·23
50	4·32	0·21
61	4·25	0·20
71	4·21	0·30
80	4·20	0·32
90	4·19	0·50
100	4·19	0·90

The Reduction of Dissolved Chlorine

Since the loss of current efficiency from discharge of hydrogen ion is only about 1% and the total current efficiency loss as given above is 4 – 10%, by far the more important part is that resulting from cathodic reduction of chlorine dissolved in the brine. This reduction may be represented thus:-

$$\tfrac{1}{2}\,Cl_2 + e \rightarrow Cl^-$$

i.e., it is a direct reversal of the main reaction at the anode which, as shown above, occurs at a potential, under cell conditions, of about +1·33V. The reduction process can occur at potentials more negative than this and, since the amalgam potential is about –1·8V., it is to be expected that it would occur in preference to discharge either of sodium ion or of hydrogen ion. The process may also be regarded as one involving a reaction between the dissolved chlorine and the sodium in the amalgam:-

$$NaHg + \tfrac{1}{2}\,Cl_2 \rightarrow Na^+ + Cl^- + Hg$$

and the net result is the same in both cases. It should be noted that the loss of chlorine in this way affects both the anode and cathode current efficiencies to the same extent.

Despite the extent of the loss of current efficiency in this way, there has been no publication of any results on works cells on the effect of such factors as current density, temperature and sodium chloride concentration, which might be expected to influence the extent of the loss. In laboratory work carried out over 40 years ago there were indications that current efficiency increased with current density and decreased with increasing sodium content of the amalgam, but it is not clear how far these conclusions can be applied to technical cells.[122,158] It may be pointed out that in the reports on the war-time German chlorine industry, as well as in those dealing with post-war mercury cell installations elsewhere, current efficiencies of 94–96% are quoted as applying at anode current densities of 0·1–0·37 amp./sq.cm.[86,113,115]

Recently, work has been done in Russia, using laboratory cells in which the chlorine formed at the anode was kept from the compartment containing the mercury cathode by means of diaphragms of sintered glass. It has been shown that in the electrolysis of pure sodium chloride solution containing 300 g./l. of sodium chloride at 25°C. and at a current density of 0·15 amp./sq.cm., a current efficiency on sodium of 99% is obtainable; on the other hand, when chlorine was present to the extent of 0·44–0·57 g./l. in the catholyte, current efficiencies of only 85·9–94·9% were obtained at 35–55°C., at 0·15 amp./sq.cm.[159] Copper and iron in the mercury, and iron in the solution, also reduced current efficiency. In a previous paper the authors showed that when chlorine or hypochlorite is present in the electrolyte, the rate of loss of sodium from the amalgam is greatly increased by stirring.[160] In the most recent publication, results are given showing the dependence of sodium current efficiency on temperature, current density and sodium concentration in the amalgam.[126] These indicate that current efficiency increases with current density and decreases with sodium concentration and temperature. Again, however, the precise bearing of these laboratory cell results on current efficiency losses from cathodic reduction of chlorine dissolved in the brine in works cells is not clear.

Losses in the Handling of Cell Products

As with the diaphragm cell process, no figures have been reported. It might be expected that the loss of sodium hydroxide would be less in the mercury cell process, since this produces a concentrated solution requiring much less further treatment than diaphragm cell liquor.

The Anode

Apart from the higher acidity of the electrolyte in the mercury cell, the corrosive conditions to which the anode is exposed are similar to those obtaining in the diaphragm cell and, for reasons similar to those already given in that connexion, graphite is now universally used as anode material. Chlorine discharge potentials on graphite and a theory for the wear of graphite under cell conditions have already been given (see page 287).

Usage of Graphite

As in the case of the diaphragm cell, a wide range of figures has been quoted for the graphite consumption. Thus values of 9–13 lb. and of 6–22 lb. per British ton of chlorine have been given in recent reviews.[2,8] However, the consumptions obtained in the most recently erected plants appear to be at the lower end of these ranges and figures of about 7 lb.[87] and 8 lb.[13,86] per British ton of chlorine have been quoted. All the figures refer to total graphite usage, which includes losses in fabrication of the anodes and losses as spent anodes.

Factors Influencing the Rate of Graphite Wear

As in the diaphragm cell, the main cause of anode wear has been assumed to be electrolytic oxidation by the reaction

$$C + 4OH^- \rightarrow CO_2 + 2H_2O + 4e$$

which gives carbon dioxide in the cell chlorine. No figures have been quoted for the loss which presumably occurs through erosion of the graphite by the mixture of brine and chlorine gas bubbles moving past its surface.

The rate of anode wear should thus depend largely on the pH of the brine in the cell, which in turn will depend on the pH of the feed brine to the cell and on the amount of hydroxyl ion liberated by discharge of hydrogen ion at the amalgam cathode. Therefore attempts have been made to reduce anode wear by adding hydrochloric acid to the feed brine, to keep the pH of the electrolyte as low as possible,[31] and in a recently erected plant provision has been made for the feed brine to be adjusted to pH 2·5.[87]

The importance of keeping the sodium chloride concentration in the electrolyte as high as possible is made clear from the results in Table XXVII.

TABLE XXVII. - EFFECT OF SODIUM CHLORIDE CONTENT OF BRINE ON CARBON DIOXIDE CONTENT OF CELL CHLORINE[115]

Feed Brine at 40°C.

Mean Sodium Chloride Content g. per l.	Cell Voltage	Carbon Dioxide in Chlorine per cent by volume
285	4·03	0·3
275	3·97	0·35
265	3·96	0·4
255	3·97	0·47
245	3·99	0·6

The effect of temperature on anode wear, as judged by the proportion of carbon dioxide in the cell gas, has also been examined but, unfortunately, only the brine feed temperatures are quoted and not the more relevant mean cell temperatures.[157] The mean sodium chloride concentration was probably about 24·5%, while the average sodium content of the amalgam leaving the cell was 0·104% by weight.

TABLE XXVIII. - INFLUENCE OF TEMPERATURE ON CARBON DIOXIDE CONTENT OF CELL CHLORINE[157]

Feed Brine Temperature °C.	Voltage	Carbon Dioxide in Chlorine per cent by volume
39	4·34	0·45
50	4·32	0·41
61	4·25	0·40
71	4·21	0·40
80	4·20	0·40
90	4·19	0·60
100	4·19	0·65

Figures have also been given for the effect of sulphate in the brine on graphite loss but the conditions of temperature, brine concentration and current density to which the results apply are not stated[115] (see Table XXIX).

In some German work a large increase in anode wear was observed when the brine contained about 14 g./l. of sodium sulphate.[161] It may be inferred from these results that sulphate at the concentration sometimes occurring in

TABLE XXIX.- EFFECT OF SULPHATE IN BRINE ON ANODE WEAR

Sodium Sulphate g./l.	Anode Wear in lb. per British Ton of Chlorine
nil	5•3
3•0	6•5
6•0	7•6
9•0	8•7
12•0	9•9
15•0	10•9

feed brine (see Table VII, page 275) may cause anode wear about 20% higher than would occur with sulphate-free brine.

No measurements appear to have been made of the effect on anode wear of chlorate, which is formed to some extent in the cell and in the plant for resaturating and purifying the cell exit brine. The reaction by which chlorate is formed appears to be:

$$NaOCl + 2HOCl \rightarrow NaClO_3 + 2HCl,$$

and the reactants are formed as a result of the slight decomposition of the amalgam in the electrolyser.[162] The chlorate appears to have little effect on anode wear at concentrations normally found, and even at 10 g./l. of sodium chlorate the effect is considered slight.[115,163]

A considerable amount of work has been done in Germany on the effect on anode wear of variation in the quality of the graphite itself.[121,164-167] By running test cells at current densities of 0•34–0•71 amp./sq.cm., a large number of different graphites were examined; the conclusion reached was that Acheson graphite was the most corrosion-resistant material and that the best German material was that prepared from German petroleum coke.[168-170]

Attempts to reduce anode wear were made in Germany during the War by impregnating the anodes with a variety of organic substances such as oils, waxes, synthetic rubbers and resins.[171] A considerable amount of destruction of the graphite was reported with some of the substances, particularly the rubbers and resins, but no information is available on the outcome of this work or as to whether impregnated anodes are used in mercury cells in other parts of the world. It may be significant, however, that there is no reference to the use of impregnation in the most modern mercury cell plants except for the protection of the metal part of the anode lead-in.[116]

The Mercury Cathode

Mercury has certain obvious advantages as a cathode. It is liquid over the whole of the range of operational temperatures. It has a fair solvent power for sodium, about 0•65% by weight of sodium dissolving at 25°C. and about 0•91% at 80°C.[172] Moreover, sodium forms compounds with the mercury with the fortunate result that it is possible to discharge sodium from the brine at an amalgam potential, as discussed above, of only about –1•8V., as compared with the normal sodium potential of –2•71V. Another advantage is that the hydrogen overvoltage on mercury is very high and this, in conjunction with the low sodium discharge potential just mentioned, means that in the working mercury cell some 99% of the current brings about sodium discharge and only 1% produces hydrogen discharge. No other liquid metal, e.g. a fusible alloy or a liquid amalgam of mercury with a considerable proportion of some cheaper metal, has yet been proposed as a substitute despite the high cost of pure mercury, 16–18/- per lb. in Britain in 1953,[173] and the large quantity needed in the cell system, some 3,500 lb. of mercury in modern cells of 30,000 ampere capacity.[86] On the other hand, a claim has recently been made that, by using a mercury cathode containing 0•001–2•0% of copper or 0•01–1•0% of silver, less hydrogen is discharged than when a pure mercury cathode is used.[174]

No figures have been reported for the loss of mercury from the cathode but such losses should presumably be small since, on electrochemical grounds, the sodium in the amalgam should be preferentially attacked. Figures are given below (see next page) for the working losses of mercury in the whole process.

The Denudation of Amalgam

The dilute sodium amalgam containing 0·1–0·2% by weight of sodium which is formed in the electrolyser reacts with water in the denuder: $NaHg + H_2O \rightarrow NaOH + \frac{1}{2} H_2 + Hg$. The amount of water used in the reaction is that required to give a concentrated solution, usually about 50% by weight, of the sodium hydroxide. Since it is possible to form sodium amalgam in the electrolyser with very little decomposition, even when the amalgam is in contact with hot brine at a pH of about 2, it is not surprising that, in the denuder, special means have to be adopted to ensure rapid and complete removal of sodium from the amalgam when this is in contact with strongly alkaline solutions. The means adopted is that of a short-circuited cell in which the anode is the amalgam, the cathode is a substance with a low hydrogen overvoltage, and the electrolyte is sodium hydroxide solution. The reaction may then be considered as occurring thus:-

$$NaHg \rightarrow Na^+ + e + Hg \text{ at the anode}$$
$$H^+ + e \rightarrow \tfrac{1}{2}H_2 \text{ at the cathode.}$$

In the modern form of denuder the amalgam is spread evenly, by means of a distributor plate, over lumps of crushed graphite held between screens and the water feed is led in at the base of the cylindrical tower.[87] The mercury is pumped back to the cell from the base and sodium hydroxide solution is removed from the top of the denuder. Similar arrangements have been described for other modern cells and for some war-time German cells; in some cases the graphite packing is flooded with amalgam[2,115] and in others it is not.[2,13,120,175,176]

Horizontal denuders have also been used in which the graphite, in the form of blocks or plates bolted together or large slotted and perforated plates, makes direct contact with the stream of amalgam in an inclined trough or pipe.[20,112] Graphite appears to be the cathode material used in all modern cells although formerly iron was used.[122]

It is clear that, by separating the anode and cathode, it is possible to carry out these reactions so as to generate electrical energy – the reversible potential being of the order of 0·8V. – and in Castner's original suggestion provision was made for using this for reducing the electrolyser voltage.[122] However, because of the high hydrogen overvoltage at the cathode, the available potential from the denuder is small at practical working rates of denudation. Also, since the current efficiency in the electrolyser is not 100%, there is insufficient sodium in the amalgam to give ions to carry all the current passing through the denuder, and so mercury ions appear in the sodium hydroxide. So the procedure was abandoned and in modern cells no attempt is made to recover electrical energy from the denuder; attention has been focused on obtaining rapid rates of denudation. Thus, in order to promote denudation, the graphite has been treated with ferric chloride or nickel chloride.[120,177] It is claimed that such treatment gives graphite ten times more active than untreated graphite.[120] Experimental use has been made of tower denuders containing pellets made by compressing a mixture of graphite and iron powders.[178] Such cathode material gives efficient denudation but is not used in full-scale denuders because of its low mechanical strength.

Studies have been made of the kinetics of amalgam decomposition in which the rates of denudation were measured by following the production of hydrogen. Borate buffers at pH 8·2–9·2 at 25°C. were used. The low reaction rates observed were attributed to the absence of impurities which catalyze the decomposition.[179] In a recent investigation the rate of reaction was found to decrease exponentially with increasing pH, according to theory, and the effect of stirring was attributed to the increase in the amalgam surface in contact with the solution.[180] A considerable amount of work has been done in Russia on the various factors affecting the rate of denudation of amalgam. Thus, at 20°C., in an atmosphere of hydrogen, the decomposition rate of sodium amalgam made from carefully purified mercury follows the kinetic law:-

$$\frac{-d[Na]}{dt} = k[Na]^{½}[OH^-]^{½}[Na^+]^{½}$$

where k is a constant, [Na] is the concentration of sodium in the amalgam in moles per litre at time t, and $[OH^-]$ and $[Na^+]$ the concentration of these ions in the solution. With initial concentrations of sodium of 0·0144 - 0·51 mole/litre, the average value of $\frac{k}{s}$ was 4×10^{-5} where s is the area of the amalgam surface.[181,182] In a study of reaction rates at 20°C. where the amalgam was stirred in contact with water, the pH being maintained at about 9 by constant addition of 0·1 N-hydrochloric acid, the concentration of the amalgam was found to decrease according to the equation:-

$$kst = 2\,(C_0^{½} - C^{½}) \;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\; \text{I}$$

s being the area, in sq.cm., of contact between amalgam and water, t the time in seconds, and C_0 and C the initial concentration, and that at time t, of sodium in the amalgam in moles/litre. The constant k was found to be $8{\cdot}7 \times 10^{-5}$ for values of C_0 between 0·27 and 0·63. When no acid was added to the water in contact with the amalgam, the time t before the concentration C of sodium was reached was given by:-

$$t = t_1 + k_2 \log \left(\frac{C_0}{C}\right),$$

where t_1 is the time given by equation I above. The constant k_2 is 324.[183]

Rates of decomposition have also been measured under conditions resembling those occurring in practice. Current densities were measured in cells made up of a 0·1% sodium amalgam anode, a graphite cathode, and aqueous solutions containing up to 750 g./l. of sodium hydroxide at 30 - 90°C. From the results it was calculated that the sodium amalgam decomposition in a solution of 750 g./l. of sodium hydroxide, with immersed graphite, at an initial temperature of 55°C. and a final temperature of 70°C. should give a current density of 0·265 amp./sq.cm. as against 0·2 amp./sq.cm. obtained under optimum conditions in practice.[184]

Studies have also been made of the catalyzed decomposition of sodium amalgam. It has been shown that the reaction between the amalgam and aqueous sodium hydroxide is catalyzed by reduced iron, vanadium, tungsten, nickel and manganese, and by alloys of iron with vanadium, tungsten, silicon, molybdenum, titanium, zirconium and boron. Salts of vanadium and tungsten also increased the reaction rate but cast iron had only a slight effect.[185] Inactivation of a ferrosilicon catalyst was shown to be caused by a suspension of iron in the mercury which covered the catalyst surface.[186] In tests with various electrode materials, iron gave a greater decomposition rate than nickel, platinum or graphite.[187]

Usage of Mercury

Little information has been published on the losses of mercury in the various parts of the process. However, an estimate of the distribution of these losses has been made from figures reported for one war-time German plant; the losses in the various stages of the process, expressed as percentages of the total loss, are:- in brine purification precipitates 65·4 - 82·1; in hydrogen from the denuder 1·6 – 2·0; in sodium hydroxide solution 0·6 – 0·75; in the air of the cell room 0·2; in the denuder graphite 0·5; as spillages 14·5 – 31·7.[19]

Total mercury usage in individual war-time plants has been reported as 0·92,[112] 0·94[112] and 1·63 lb.[120] per British ton of chlorine. For the most modern plants, figures of 0·22,[13] 0·28[86] and 0·63 lb.[87] have been given.

Hydrogen

Hydrogen from the denuders may be water-cooled, either by direct scrubbing[19] or in a heat exchanger,[19,87] and may then be dried by sulphuric acid in a packed tower.[19] The gas contains a small amount of mercury which may be removed by scrubbing with chlorine water[19] or chlorinated brine,[2] or by refrigerating and filtering, first through cotton wool and then through active carbon.[10,112] The mercury content of the gas after filtration through cotton wool is given as 30 – 50 micrograms per cu.m.[112] and, after treatment with active carbon, as less than 1 microgram per cu.m.[10,112] The purified gas is used for the production of ammonia[2,13] and hydrochloric acid,[77,87] for the hydrogenation of oils,[2] as a fuel,[86] and in various inorganic reductions (see page 290).

Chlorine

The chlorine from mercury cells contains the same range of impurities as that from diaphragm cells with the important difference, however, that the hydrogen content of mercury cell chlorine is higher and more variable. The purification and liquefaction of mercury cell chlorine recently described for modern cell plants[13,87] is closely similar to the procedure described in detail above for diaphragm cell chlorine but, for the reason just given, greater attention has to be paid to the hydrogen content of the purge gas from the liquefaction of mercury cell chlorine.

Sodium Hydroxide

The caustic soda solution produced in modern mercury cells normally contains up to 50% by weight of sodium hydroxide, although concentrations as high as 73% have been obtained.[10,13] The product may contain suspended graphite[10,87,112] and mercury,[10] these being removed by filtration through porous carbon tubes[87,112] which may be coated with a cellulose filter-aid,[87] or through sintered nickel powder.[10] After filtration, the purity is such that the solution may be used in the rayon industry without further treatment.[87]

Further concentration of the cell product is not usual[18,78,87] but, where solid sodium hydroxide is required, the 50% solution is evaporated to about 75% concentration in forced circulation evaporators.[99] This concentrated solution, or the 70 – 73% product from the cells, is then evaporated in open pots as described earlier (see page 292).

A typical analysis of sodium hydroxide solution from mercury cells is given in Table XXX.

Mercury cell sodium hydroxide solution may be shipped in steel drums or in road or rail tanks.[99] The solid product is normally packed in thin sheet steel drums.[99]

COST OF CHLORINE MADE IN DIAPHRAGM AND MERCURY CELLS

No detailed figures have been published giving the cost of production of chlorine in the most modern American or British diaphragm or mercury cell plants. Manufacturing cost estimates have been given relating to production in January 1947, under U.S. conditions, in Hooker Type S diaphragm cells operating at 8,000 amp. and in German 7-metre long mercury cells operating at 13,000 amp.[2] It was concluded that the capital costs for the two processes were closely similar. The manufacturing costs per pound of chlorine

TABLE XXX. - ANALYSIS OF MERCURY CELL SODIUM HYDROXIDE SOLUTION[2]

Constituent	%
$NaOH$	50·00
Na_2CO_3	0·10 – 0·20
Na_2SO_4	0·0004 – 0·0020
$NaCl$	0·001 – 0·002
CaO	0·001 – 0·002
MgO	0·0001
Al_2O_3	0·0010 – 0·0012
SiO_2	0·0010 – 0·0030
Fe	0·0001 – 0·0008
Cu	0·0002
Hg	$<10^{-6}$

(excluding the value of the sodium hydroxide also produced, which, in the case of diaphragm cell production, was considered to require special purification) were 2·77 cents for diaphragm cells and 2·63 cents for mercury cells. If the diaphragm cell sodium hydroxide was of ordinary grade and not specially purified, the production cost of chlorine in this cell was slightly less than that from the mercury cell.[2] Manufacturing costs for a modern Italian mercury cell plant have recently been published.[13]

The selling prices of chlorine in large quantities in the U.S.A. and in Britain in 1953 were about 3 cents[188] and 3·5 pence[173] per lb. respectively.

SUMMARY OF OPERATING DATA FOR DIAPHRAGM AND MERCURY CELLS

Some of the important data for the most modern diaphragm and mercury cells are summarized in Table XXXI. The values listed are taken either from the text above or from recent publications on the two processes.[2,13,86,87,115]

TABLE XXXI. - TYPICAL OPERATING DATA FOR MODERN DIAPHRAGM AND MERCURY CELLS

	Unit	Diaphragm Cells	Mercury Cells
Cell capacity	amperes	20000	30000
Cell capacity	lb. Cl_2/day	1350	2000
Anode current density	amp./sq.cm.	0·092	0·48
Cathode current density	amp./sq.cm.	0·083	–
Current efficiency	%	96·8	94 – 96
Cell voltage	volts	3·65	4·3 – 4·5
Energy consumption	kw.hr./British ton Cl_2	2896	3472 – 3620
Energy efficiency	%	58	48·4 – 46·3
Potential drop through diaphragm	volts at 0·068 amp./sq.cm.	0·12 – 0·15*	–
Cell temperature	°C.	95	65 – 70
Mercury charge in cell	lb.	–	3500
Mercury loss	lb./British ton Cl_2	–	0·22 – 0·63
Graphite consumption	lb./British ton Cl_2	7 – 8	7 – 8
Sodium chloride content of inlet electrolyte	% by weight	26·8	26·0
Sodium chloride content of exit electrolyte	% by weight	14 – 15	22·8 – 24·4

Table XXXI (continued)

	Unit	Diaphragm Cells	Mercury Cells
Composition of chlorine:			
Chlorine	% by volume	96·67	97–98
Hydrogen	% by volume	0·14	0·5–1·0
Carbon dioxide	% by volume	1·77	0·5–1·5
Composition of sodium hydroxide solution:			
NaOH	% by weight	50·00	50·00
Na_2CO_3	% by weight	0·10–0·30	0·10–0·20
Na_2SO_4	% by weight	0·013–0·020	0·0004–0·0020
NaCl	% by weight	1·00	0·001–0·002
$NaClO_3$	% by weight	0·05–0·10	–
CaO	% by weight	0·0017	0·001–0·002
MgO	% by weight	0·001–0·002	0·0001
Al_2O_3	% by weight	0·0013–0·0030	0·0010–0·0012
SiO_2	% by weight	0·018–0·025	0·001–0·003
Fe	% by weight	0·0005	0·00001–0·00008
Cu	% by weight	0·00003	0·0002
Hg	% by weight	–	$<10^{-6}$

* These values refer to older types of diaphragm cell.

THE ELECTROLYSIS OF FUSED SODIUM CHLORIDE

Chlorine is obtained as a by-product from the electrolysis of fused sodium chloride in the manufacture of metallic sodium. The only part of the process described here in detail is that concerned with the recovery of the chlorine. The process is briefly the electrolysis, at about 590°C. in cells of 24,000–32,000 amp. capacity, of a molten mixture of about 60% by weight of calcium chloride and 40% of sodium chloride, the calcium chloride being added to obtain a low melting point electrolyte.[189] Molten sodium is produced at the steel cathode and chlorine at the graphite anode. The cell voltage is about 7V. and the energy consumption for the process is equivalent to about 7900 kw.hr. per ton of chlorine.[190] This energy is therefore more than twice that required for making chlorine by the electrolysis of brine. The amount of by-product chlorine made in this way is important, the U.S.A. output being about 149,000 tons in 1950.[4,191] A figure of 185,000 tons for world production for 1951 may be derived from an estimate which has been given for world production of sodium in that year, 120,000 metric tons, on the assumption that all the sodium was made by the electrolysis of sodium chloride.[190]

A very pure sodium chloride is required if cell operation is to be satisfactory[190] and this naturally favours the production of pure chlorine. The hot chlorine, which entrains a small proportion of calcium chloride and sodium chloride from the electrolyte, is collected at the top of the cell in a brick-lined nickel dome kept under a suction of about 5 mm. of water to avoid leakage of chlorine. From the dome the gas passes into a steel pipe with a short horizontal section adapted for easy removal of the deposited electrolyte dust; from this point the chlorine passes into one or other of two collecting mains, one for concentrated chlorine and the other for the dilute gas.[189] The gas then passes to two stoneware water scrubbing towers in series where the remaining entrained electrolyte dust is removed, and also silicon tetrachloride, presumably derived from the brickwork in the cell.[19] The concentrated wet chlorine is then dried by sulphuric acid and liquefied in the conventional way (see page 291).[192] Any weak chlorine produced during cleaning of the pipe mains, along with weak gas from the liquefaction of the concentrated chlorine,

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is absorbed to form hypochlorite.[189]

No report has been found giving a typical analysis of this by-product chlorine from sodium manufacture; it presumably differs from chlorine made in brine cells in that it may contain silicon tetrachloride but, since the anodes are not impregnated, it may contain less chlorinated organic substances.

MISCELLANEOUS PROCESSES FOR THE MANUFACTURE OF CHLORINE

As already shown, the electrolysis of brine and of fused sodium chloride gives the great bulk of the chlorine manufactured to-day; the remainder is produced by a wide variety of processes, the salient features of which are summarized below. It has been estimated that by 1960 the United States output of chlorine by these miscellaneous routes, as well as by the electrolysis of fused sodium chloride already described, may reach 200,000 tons per year.[193]

THE OXIDATION OF HYDROCHLORIC ACID

This process, the Deacon process (Mellor,II,31), was widely used in the 19th century. It became obsolete after the development of the more economical electrolytic routes, but recently attempts have been made to improve it, in order to deal with the large amounts of hydrochloric acid - estimated at 500,000 tons per year in the United States[193] - which are available as a by-product from organic chlorinations of the type:-

$$RH + Cl_2 \rightarrow RCl + HCl.$$

Because of the advantage of having the main raw material at almost zero cost, various manufacturers have carried out fresh research on methods of improving the original Deacon process, which may be written:-

$$4\,HCl + O_2 \rightarrow 2\,Cl_2 + 2\,H_2O.$$

The fundamental problem in the process is to obtain high reaction speeds at the low temperatures at which the equilibrium is favourable for chlorine production. In recent years improvements have been claimed in the process, particularly for the catalyst required in the reaction, and proposals have been made to use the chlorides and oxides of multivalent metals,[194] chromium oxide supported on titanium oxide,[195,196] special reaction and regeneration using a copper catalyst,[197,198] copper chloride promoted by lead chloride,[199] and metal oxides such as iron oxide[200] instead of the copper chloride used in the original Deacon process.

A plant using an improved catalyst and reduced working temperatures, producing 35 tons of chlorine per day, was expected to be working in the United States by the end of 1953.[193] In the first stage of this process hydrochloric acid and ferric oxide in potassium chloride react as follows:-

$$6HCl + Fe_2O_3 = 2FeCl_3 + 3H_2O;$$

while in the second stage the mixture of ferric chloride and potassium chloride is air-blown:-

$$2FeCl_3 + \tfrac{3}{2}\,O_2 = Fe_2O_3 + 3Cl_2.$$

In another plant, operated recently on a pilot scale, a similar process is carried out. Operation at low temperature is claimed as well as almost complete utilization of the hydrochloric acid without the necessity for recycling.[193]

A similar process coupled with absorption of the chlorine in sulphur monochloride has been used in Germany[201] and during the last war a pilot plant was run at Oppau with an output of 10 tons of chlorine per day.[202] This plant used a molten mixture of potassium chloride and ferric chloride as catalyst; agitation of the catalyst by the incoming gases was claimed to be advantageous.[202]

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A comparison of the construction and operating costs of the Oppau plant with those for the electrolysis of hydrochloric acid at Bitterfeld indicated that, for large plants, the chemical oxidation process would be cheaper.[202]

THE ELECTROLYSIS OF HYDROCHLORIC ACID

This process, like the recently revived Deacon process, depends economically on the availability of cheap by-product hydrochloric acid. It consists in the electrolysis of the acid in a cell similar in principle to the diaphragm cell already described (see page 276) for the electrolysis of sodium chloride solutions. Thus in an early proposal, hydrochloric acid solution flows through a cathode chamber in which the hydrogen is discharged and then through the anode chamber in which the chlorine is liberated, means being provided for dechlorinating the exit acid, increasing its concentration of hydrochloric acid, and returning it to the cell.[203]

The development in Germany of a cell employing bipolar electrodes has been described[204] as well as means of maintaining the acid concentration in the electrolyte.[205] This work led to the installation of a cell which ran successfully at Bitterfeld and later for over a year at Wolfen; this cell has been described in detail.[206,207] It consists essentially of bipolar graphite electrodes, separated by diaphragms made of polyvinyl chloride cloth, and held together by an outer frame made of steel lined with Haveg or rubber in an arrangement like a filter press. The area of graphite electrode in each unit cell was normally about 1·4 sq.m., the graphite was smooth on the anode side and the diaphragm was filled with broken graphite in pieces up to 1·5 cm. size; in operation these pieces of broken graphite form a high surface-area anode and the resulting reduction in current density contributes to a low cell voltage. Movement of the hydrochloric acid is from anode to cathode. Hydrochloric acid of 32% concentration was fed to the cell at such a rate that the outlet acid contained 10% of hydrochloric acid. With 1000 amp., at a nominal current density of about 0·07 amp./sq.cm., the cell worked at 80–90°C., at a voltage of 2·3V., and a current efficiency of 92–94%. The loss of current efficiency is attributed to cathodic reduction of the chlorine dissolved in the hydrochloric acid passing from the anode to the cathode compartment, as well as to some current leakage. The factors leading to the voltage of 2·3V., which is approximately 1V. higher than the reversible voltage for the cell, are not discussed. Both the chlorine and hydrogen are contaminated with hydrochloric acid, and are purified by scrubbing with water. The washed anode gas contains about 99·5% of chlorine and 0·2–0·4% of carbon dioxide.[206] The presence of this proportion of carbon dioxide in the cell gas is surprising in view of the high acidity of the anolyte (see page 287). However, this is confirmed in the report on the process by the statement that the pieces of anodic graphite are slowly consumed and have to be replenished after about three months; the usage of scrap graphite for this purpose is said to be 2·2 lb. per British ton of chlorine.[206]

It is not known whether there have been further developments of this direct electrolysis of hydrochloric acid, but some of the difficulties in operation have led to proposals for a two stage process, based on the electrolytic reduction of cupric chloride rather than hydrochloric acid.[193] The reduced cupric chloride is oxidized by air and hydrochloric acid and then recycled to the electrolysis stage.[208] A claim has been made that the copper chloride cell can be operated at current densities up to 0·27 amp./sq.cm. and at voltages as low as 0·72V., and accounts have been given of the plant required.[209-211] Chlorides of metals other than copper have been tried but none has been found to be so suitable. A pilot plant has been designed and operated using this process which, at a current density of 0·11 amp./sq.cm., uses 0·4 kw.hr. of energy per lb. of chlorine compared with 0·8 kw.hr. for the direct electrolysis of hydrochloric acid. It is considered, however, that it is more economical to work the copper chloride electrolysis at a current density of 0·43 amp./sq.cm. and, where electrical energy costs are low and by-product hydrochloric acid is available, this route is said to compare well with other processes.[193]

ELECTROLYSIS OF MISCELLANEOUS CHLORIDES

Chlorine may be produced by the electrolysis of ferrous chloride either alone[212] or in concentrated solutions of sodium chloride, calcium chloride, or other chloride of a metal which forms only one chloride.[213] As a by-product, it may also be obtained in the production of zinc by electrolysis of a solution of zinc chloride in a mercury cell.[214,215] A diaphragm cell for the production of chlorine and chromous chloride from chromic chloride has been described.[216] A patent has been granted for the production of ammonia and chlorine by the electrolysis of solutions of ammonium chloride containing the chloride of an alkali metal or alkaline earth metal.[217] A cell for the electrolysis of ammonium chloride solutions having an asbestos paper diaphragm, a perforated steel cathode, and a graphite anode has been described.[218] It was operated at 50 – 75°C. at an anodic current density of 0·145 amp./sq.cm. and a cathode current density of 0·11 amp./sq.cm. The cathode current efficiency was 84%, but 36% of the chlorine liberated at the anode entered into side reactions, and explosions occurred in some cases. Chlorine is also obtained in the electrolysis of magnesium chloride, available in bittern.[193] No records have been found indicating the amount of chlorine produced at present by any of these routes, but it is presumably small.

There are records, however, which give the amount of chlorine made in certain other electrolyses. Thus in the electrolysis of aluminium chloride solution at Ludwigshafen in Germany during the last war, about 14 tons per month of chlorine was made.[219] The process was carried out in a rubber-lined cell fitted with graphite anodes and cathodes and having a diaphragm of blue asbestos cloth. The chlorine made was said to have a purity of 99·8 – 99·9%.

A considerable amount of chlorine is obtained as a by-product in the manufacture of potassium hydroxide by the electrolysis of potassium chloride solutions. In Germany, potassium hydroxide was produced either in mercury or in diaphragm cells in seven different plants.[220] The scale of production of by-product chlorine from this source is not stated explicitly but appears to have been of the order of 50,000 tons per year during the 1939-45 war.[19,77,220] Figures for the output of French potassium hydroxide indicate that the equivalent production of chlorine in 1951 was about 26,500 tons.[221]

Detailed information is available on the types of mercury cell used in Germany during the war.[220] These present no noteworthy differences from the cells described above for the electrolysis of sodium chloride solutions. In operation, the potassium chloride solution has to be purified in the manner described for sodium chloride solution, care being taken to ensure that magnesium, chromium and vanadium are absent, and that the aluminium and iron contents are low. The anode-cathode gap in the cell is made greater than in sodium chloride electrolysis, in order to minimize loss of current efficiency through cathodic reduction of the chlorine. On 12,000 amp. cells operating at 0·24 amp./sq.cm. with an exit brine temperature of 75 – 80°C., and inlet and exit potassium chloride concentrations of 345 – 350 and 270 – 280 g./l. respectively a voltage of 4·3V. was obtained and a current efficiency of 92 – 94%. The hydrogen content of the chlorine was 1·5 – 2·0%, somewhat higher than in sodium chloride cells. The purification and subsequent treatment of the chlorine follow the lines indicated above under mercury cells.

In Germany, Billiter diaphragm cells were used for the electrolysis of potassium chloride solutions but no details have been made available.[19,77,220]

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THE REACTION BETWEEN SODIUM CHLORIDE AND NITRIC ACID

This process, as already pointed out, was expected to give just over 1% of the U.S.A. output of chlorine in 1953. The process was investigated over 25 years ago,[222,223] and its economics, as well as the detailed reactions involved, received attention shortly afterwards.[224] In 1938-1941 a series of patents was granted to the Solvay Process Co. (now the Allied Chemical Corporation), the only company operating this process.[225-233] These patents cover various features of the process, which is carried out in two stages. A slurry of 65% concentrated nitric acid and sodium chloride reacts to give nitrosyl chloride, chlorine, and sodium nitrate solution, according to the equation:-[193]

$$4\ HNO_3 + 3\ NaCl = NOCl + Cl_2 + 3\ NaNO_3 + 2\ H_2O.$$

The sodium nitrate solution is evaporated, crystallized and filtered to give the solid nitrate, while the chlorine is fractionated from the nitrosyl chloride, which is then oxidized by air to give a further amount of chlorine according to the reaction:

$$2\ NOCl + O_2 = 2NO_2 + Cl_2.$$

Alternatively the nitrosyl chloride may be converted into nitric acid.[234] The process requires cheap salt and nitric acid and a ready market for the sodium nitrate, which is used mainly as a fertilizer. Although the process has been studied in Russia as a prospective route to chlorine,[235] the only plant known to be in operation is at Hopewell, Va., U.S.A. and this has recently been increased in capacity to give 75 tons of chlorine daily. Corrosion problems, which are serious, are said to have been solved.[193]

THE REACTION BETWEEN SODIUM CHLORIDE AND SULPHUR TRIOXIDE

As early as 1920-23, patents were obtained for chlorine production by reaction between sodium chloride, sulphur dioxide and air at 500°C. or higher temperatures, in a rotary inclined furnace.[236,237] It was stated that thionyl chloride could be obtained by using an excess of sulphur dioxide. According to more recent work, sodium chloride and gaseous sulphur trioxide react to form addition compounds containing 1, 2 and perhaps 3 moles of sulphur trioxide per mole of sodium chloride.[238] These reactions are stated to be impeded by crust formation and the higher addition compounds are unstable at room temperautre. Reactions at higher temperatures have been studied also.[238] Thus above 115°C., $NaCl,2SO_3$ decomposes:-

$$NaCl,2SO_3 \rightarrow NaSO_3Cl + SO_3;$$

while between 225° and 300° the reaction occurring is:

$$3\ NaSO_3Cl \rightarrow Na_2S_2O_7 + NaCl + Cl_2 + SO_2.$$

Above 330° the following reaction occurs:-

$$2Na_2S_2O_7 + 2NaCl \rightarrow 3Na_2SO_4 + Cl_2 + SO_2.$$

The kinetics of the last two of these reactions have been investigated and consideration has been given to a technical process based on them.[238] Since 1942 there have been certain claims for improvements in the operation of the process.[239-243] Further fundamental work has also been done[244] and fresh appraisals of the commercial prospects have been made.[193,245] The unfavourable factors in the process are the large heat requirements, the side reactions, and the difficulty in obtaining complete decomposition of the sodium chlorosulphonate. The high corrosion rate of the plant, the problem of separating the chlorine and sulphur dioxide and the fact that approximately two tons of sodium sulphate and one ton of sulphur dioxide are made for every ton of chlorine, are formidable additional obstacles, and up to 1953 the process has been worked only on the pilot scale.[193]

THE REACTION BETWEEN HYDROCHLORIC ACID AND SULPHUR TRIOXIDE

This process is similar to that just described, but using by-product hydrochloric acid in place of sodium chloride and obtaining sulphuric acid instead of sodium sulphate. The various stages in the process have been described.[193] The first step is the formation of chlorosulphonic acid, which occurs at 70–100°C.:-

$$SO_3 + HCl \rightarrow SO_3HCl.$$

This is decomposed at 200–300°C.:-

$$2SO_3HCl = SO_2Cl_2 + H_2SO_4,$$

while at about 200°C. the sulphuryl chloride decomposes to give sulphur dioxide and chlorine:-

$$SO_2Cl_2 = SO_2 + Cl_2.$$

While the process appears to be more promising than the sodium chloride-sulphur trioxide route in several respects, it was reported in 1953 that it had not been operated even on the pilot scale in the U.S.A.[193]

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SECTION XIII

THE PHYSICAL AND CHEMICAL PROPERTIES OF CHLORINE

By F. W. KIRKBRIDE

GENERAL PHYSICAL PROPERTIES

Density and Specific Volume of the Gas. Equations of State.

Ross and Maass determined the density over the range 15 – 75°C., at up to 2 atm. pressure. The carefully purified gas was handled in an all-glass apparatus having taps lubricated with a mixture of meta- and ortho-phosphoric acids. The temperature was controlled to 0·02°C. The weight of gas in the measuring vessel was determined by condensing the gas in a bulb which was afterwards sealed and weighed. To find the volume of the vessel, the amount of pure sulphur dioxide filling it at a known pressure was determined. The effect of temperature on the volume of the bulbs was allowed for.

A selection of the results obtained is given in Table I, in which the extent of deviation from the simple gas laws is indicated by the apparent molecular weight, derived from the absolute density by the relation $M' = wRT/PV$, where w is the mass of gas occupying the volume V (theoretical molecular weight is 70·91).

TABLE I. - DENSITY AND APPARENT MOLECULAR WEIGHT OF CHLORINE

Pressure mm.	Absolute density mg./c.c.	M′	Pressure mm.	Absolute density mg./c.c.	M′
15·00°C.			50·00°C.		
261·9	1·037	71·18	204·9	0·7236	71·15
497·3	1·980	71·56	498·6	1·766	71·36
752·1	3·003	71·76	751·9	2·673	71·63
1293	5·217	72·49	1286	4·598	72·03
1603	6·508	72·97	1534	5·509	72·36
35·00°C.			75·00°C.		
236·1	0·8738	71·13	254·1	0·8317	71·08
492·9	1·832	71·43	489·5	1·606	71·25
750·9	2·804	71·76	755·9	2·486	71·39
1234	4·646	72·36	1280	4·232	71·78
1593	6·014	72·54	1525	5·052	71·93

These results fit, within an average deviation of 0·04%, the equation:-

$$d' = \frac{0{\cdot}86427\,P}{T}\Big[1 + \Big\{\frac{2515 - 2{\cdot}991(T+199)}{T^2}\Big\}P + 2\Big\{\frac{2515 - 2{\cdot}991(T+199)}{T^2}\Big\}^2 P^2 + \dots\Big],$$

where d' is the observed density (now in g./c.c.), P is in atm., and T is in °K. (This equation was obtained from an earlier equation of state developed by Maass).[1]

The equation for d' gives values agreeing closely with what are probably the most accurate of earlier determinations, namely 0·003063 g./c.c. at 0°/725 mm. and 0·002896 g./c.c. at 15°/725 mm., by Jaquerod and Tourpaian.[2] Also, when extrapolated beyond the temperature range of the above measurements, the equation gives values of d' close to those earlier found by Pier,[3] as is illustrated in Table II.

TABLE II. - COMPARISON OF VALUES FOR THE DENSITY OF CHLORINE

Temperature °C.	Pressure atm.	Absolute density (10^{-3} g./c.c.)	
		Ross & Maass equation	Found by Pier
99·95	0·1370	0·3176	0·3174
100·40	1·0000	2·327	2·324
100·40	1·3822	3·224	3·217
150·70	1·0000	2·046	2·044
184·00	1·0000	1·896	1·894
184·50	1·6960	3·217	3·215

A rather simpler formula, stated to be valid for calculating the molecular volume of chlorine at pressures up to about 8 atm., is:-

$$V = \frac{RT}{p} + 39 - \frac{8{\cdot}5 \times 10^{8}}{T^{2{\cdot}6}} \quad \text{c.c./mole.}^{4}$$

Another equation of state, claimed[5] to represent to within 1% the behaviour of chlorine over the entire range of the stable gaseous condition below the critical temperature, has the form:-

$$p = \frac{RT}{v-b} - \frac{a'}{Tv(v-b)} + \frac{c'}{T^{4/3}v^{3}}.$$

If π, θ and ϕ are respectively the pressure, temperature and molecular volume expressed as fractions of the corresponding critical values, the equation becomes:-

$$\pi = \frac{3{\cdot}75\theta}{\phi - \frac{1}{4}} - \frac{6}{\phi\theta(\phi - \frac{1}{4})} - \frac{4}{\theta^{4/3}\phi^{3}}$$

(critical temperature and pressure taken as 416°K. and 78 atm. respectively; critical volume not stated). Above the critical temperature, these equations give the pressure within 2% for $\phi = 1$ to 1·7 and $\theta = 1$ to 1·75.

Nernst's equation of state, $p(v - v_l) = RT\,[(1 - (p/p_c^{\cdot}))]$, where p is the pressure in atm., p_c is the critical pressure (atm.), v and v_l are respectively the molecular volumes of the gas and liquid in litres, and $R = 0{\cdot}08207$, is valid within about 7% for chlorine at 0 – 70°C.[6]

Haggenmacher[7] gives for the saturated vapour of chlorine in the range 0 – 144°C. the equation of state:-

$$p = \frac{CT}{v + 1{\cdot}4265} - \frac{0.31935}{T(1.4265)^{2}}$$

where p is in atm., T in °K., and v in litres He does not state a value for C.

Ziegler gives for the specific volume of the saturated vapour the equation

$$v = \frac{11{\cdot}956\,T}{P} - \frac{0{\cdot}04473}{(T/100)^{2{\cdot}21}} - \frac{2{\cdot}3596P^2}{(T/100)^{6{\cdot}25}10^{11}}$$

where v is in l./g., T in °K., and P in kg./m.^{2} (the third term is negligible below $P = 10^4$, i.e. 8 atm.). Some of his values calculated for v are:-

Temp. (°C)	−70	−35	0	20	40	60
v(c.c./g.)	1563	279·6	81·89	46·77	28·66	18·44

Temp. (°C)	80	100	120	140	144(critical)
v(c.c./g.)	12·20	8·082	5·169	2·842	1·763

Hulme and Tilman derived a still more complex equation of state: v (saturated vapour) $= 82{\cdot}055\ T/p + 39{\cdot}0 - 122{\cdot}47 \log P + 0{\cdot}94\ P^{1{\cdot}15} - 8{\cdot}5 \times 10^8/T^{2{\cdot}6} - 4{\cdot}9 \times 10^{-10}\ P^{6{\cdot}0}$, where v is in c.c./mole, P in atm. and T in °K. This equation was claimed to be valid up to $P = 75$ atm., and was used to prepare a table of values of v, in British units, over the range from −50°F. up to 291·2°F.[9]

In a subsequent paper,[10] Hulme gave a table of specific volumes of superheated chlorine at various temperatures and pressures, from which the values reproduced in Table III are selected.

TABLE III. - SPECIFIC VOLUME OF SUPERHEATED CHLORINE

Pressure (abs.) lb.per sq.in.	Specific Volume (cu.ft./lb.) At temperatures (°F.)					
	0	50	100	200	300	400
10	6·872	7·641	8·410	9·947	11·475	12·991
30	—	2·495	2·761	3·292	3·812	4·324
50	—	1·466	1·632	1·961	2·279	2·590
80	—	—	0·9957	1·211	1·416	1·614
120	—	—	0·6416	0·7934	0·9357	1·070
200	—	—	—	0·4568	0·5496	0·6327
300	—	—	—	0·2861	0·3540	0·4114
400	—	—	—	0·1986	0·2550	0·3024

It is to be noted that, apart from Ross and Maass, the authors of the various equations of state given above did not make independent determinations of the vapour density of chlorine, but made use of the data provided by the earlier workers quoted in Mellor, II, 48.

London found that the molecular attractions in chlorine, causing it to depart from the ideal gas laws, could be accounted for quantitatively by considering the periodic dipoles set up by motion of the chlorine nuclei and electrons in the electric fields due to one another, e.g. he calculated for the quantity a in the Van der Waals equation the value 680×10^4 atm.cm.^{6}g.$^{-2}$ (experimental value 632 in same units).[11]

It has been stated[12] that the density of chlorine at ordinary temperatures indicates the presence of some molecules heavier than Cl_2, e.g. Cl_4, but there is no real evidence for this. It seems sufficient to account for the unduly high density by postulating the molecular attractive forces just referred to.

Several authors have suggested the existence of a triatomic molecule Cl_3 as an intermediate in chain reactions involving chlorine. This is discussed in the sub-section on chemical properties (see page 384).

Thermal Dissociation of Chlorine.

Older measurements of the vapour density and heat capacity of chlorine indicated that the molecules begin to be dissociated into atoms above 600°C., or at least above 1200° (Mellor, II, 48,55). More definite evidence has since been obtained in the following ways.

Refs. p. 333

By measurement of the pressure developed in a porcelain bulb containing chlorine and heated to various temperatures, and comparison with the pressure changes observed in the same bulb when filled with nitrogen, the degree of dissociation at approximately 1 atm. was estimated by Trautz and Stäckel to be 1·50% at 1200°C., 2·10% at 1240°, and 3·05% at 1280°, corresponding to a heat of dissociation of 71 ± 3 kg.-cal./mole.[13]

By chemical estimation of the weight of chlorine occupying a bulb of known volume at various temperatures, Trautz and Geissler found that log K_p (= log $p^2_{\text{Cl}}/p_{\text{Cl}_2}$) had values rising from −1·85 at 1151°C. to −1·17 at 1264°, the derived heat of dissociation being 59·5 ± 2kg.-cal./mole.[14] A later recalculation of these results gave values of log K_p rising from −1·899 to −1·168, with 57·1 ± 2·1 kg.-cal./mole as the heat of dissociation.[15] By a similar method, but comparing the amounts of chlorine and carbon dioxide required to fill a vessel at 1478°K. (1205°C.), the value of log $K_{p(\text{atm.})}$ was found by von Wartenberg and Weigel to be −2·50 ± 2, the proportion of molecules dissociated being 2·8%.[16]

By working at pressures around 10^{-3} atm., Henglein was able to make measurements at rather lower temperatures. The dissociation was followed by pressure changes deduced from observations of the rate of damping of a quartz fibre vibrating in the gas. The degree of dissociation was found to rise from 18% at 985°K. (712°C.) to 60% at 1151°K. (878°C.), the corresponding heat of dissociation being 54 kg.-cal./mole. The expression found[17] for the variation of equilibrium with temperature was:-

$$\log K_{p(\text{atm.})} = -\frac{54000}{4{\cdot}571\,T} + 1{\cdot}75\,T - 4{\cdot}09 \times 10^{-4}\,T + 4{\cdot}726 \times 10^{-8}T^2 + 0{\cdot}93.$$

An alternative technique, used by Wohl, was to derive the degree of dissociation of chlorine from measurements of the temperature rise on explosion of mixtures of hydrogen and chlorine containing an excess of either reactant, or added hydrogen chloride; the liberation of chlorine atoms leads to a lower maximum temperature than would otherwise be the case. The values found for the degree of dissociation (x) were as follows:

Temperature, °C.	800	1000	1200	1500	1700	2000	2300
x, %	0·051	0·445	2·18	12·0	27·2	59·4	86

The calculated heat of dissociation was 57 ± 2kg.-cal./mole at 0°K. and constant volume.[18,19]

Giauque and Overstreet later derived more precise values for the equilibrium constant by calculations based on spectroscopic data for the energy of of vibration, rotation and dissociation of the chlorine molecule. The minor effects due to isotopic atoms of chlorine were taken into account. Values found for K_p at various temperatures were as follows:-

Temperature, °K.	298·1	500	1000	1500
K_p, atm.	$1{\cdot}95 \times 10^{-37}$	$2{\cdot}70 \times 10^{-20}$	$1{\cdot}71 \times 10^{-7}$	$3{\cdot}68 \times 10^{-3}$
Temperature, °K.	2000	2500	3000	
K_p, atm.	$5{\cdot}69 \times 10^{-1}$	11·99	92·21	

In these calculations, the value taken for ΔE°_0, the heat of dissociation at 0°K. and constant volume, was 56·9 kg.-cal./mole. The original paper also lists many values for $\Delta G^\circ/T$, the free-energy function of the dissociation at various temperatures.[20]

Using a more recent value for ΔE°_0, namely 57·194 kg.-cal./mole, and revised values of the fundamental constants *h* and *k*, Butkov has calculated rather lower values for K_p as follows:[21]

Temperature, °K.	298·1	500	1000	1500
K_p, at.*	$1{\cdot}17 \times 10^{-37}$	$1{\cdot}97 \times 10^{-20}$	$1{\cdot}46 \times 10^{-7}$	$3{\cdot}25 \times 10^{-3}$

Temperature, °K.	2000	3000
K_p, at.*	$5{\cdot}19 \times 10^{-1}$	87·6

*1 at. = 1 kg./sq.cm. = 0·967841 atm.

In addition to the high-temperature dissociation, there is a very questionable allegation that the values of the vapour pressure and surface tension of chlorine, and of the freezing-points of its solutions in several solvents, indicate that the molecules in the liquid state are dissociated into atoms as the temperature falls from the normal boiling-point to −103°.[22]

For the dissociation of the chlorine molecule by the absorption of light the reader is referred to the section on the chlorine spectrum (see page 627). Here it will suffice to mention that in a very recent review of spectroscopic dissociation energies, the value for Cl_2 is taken as 57·08 kg.-cal./mole, or 2·746 e.V.[23] Dissociation of the molecule by electric discharge, and factors influencing the rate of recombination of chlorine atoms, are dealt with in the sub-section on chemical properties (see page 383).

Density of Liquid and Solid Chlorine. Atomic Volume.

The following values were found by Kanda for the density of liquid chlorine:[24]

Temperature, °K.	208·00	210·51	215·60	220·61	227·90
ρ, g./c.c.	1·643	1·636	1·621	1·605	1·580

Temperature, °K.	235·50	239·96
ρ, g./c.c.	1·555	1·530

These figures were combined by Ziegler with those of earlier workers (Mellor, II, 49) to give a table[8] of the density and specific volume for every 5°C. from −70° up to the critical point. A selection of the values is given in Table IV.

TABLE IV. - DENSITY AND SPECIFIC VOLUME OF CHLORINE

Temperature, °C.	−70	−35	0	20	40	60	80
ρ, g./c.c.	1·6552	1·5649	1·4680	1·4085	1·3450	1·2760	1·1991
Sp.Vol.c.c./g.	0·6042	0·6390	0·6812	0·7100	0·7435	0·7837	0·8339
Temperature, °C.	100	120	140	144 (critical)			
ρ, g./c.c.	1·1099	0·9962	0·7921	0·5672			
Sp.Vol. c.c./g.	0·9010	1·0039	1·2624	1·7631			

A table of the density of liquid chlorine in lb./cu.ft. for every 5° or 10°F. from −50°F. up to the critical point is also available.[9]

Herz[25] found that Pellaton's values for the density of liquid chlorine (Mellor, II, 50) are expressible with fair accuracy by the equation $(d-d_c)/a(t-t_c)^b = 1$, where d_c = 0·573 g./c.c., t_c = 144°C. and *a* and *b* have respectively the values 0·10186 and 0·43880.

The density of solid chlorine at −195°C. was found[26] by means of a volumenometer to be 2·13 g./c.c., corresponding to an atomic volume of 16.66 c.c., or 16·3 c.c. at 0°K. when extrapolated by a (calculated) expansion coefficient of 30×10^{-5}. The same value for 0°K. was obtained by a calculation according to an empirical rule connecting the density at 0°K. with that at the b.p.[27] Another value for the atomic volume at −195°C, is 16·7 c.c.[28]

Crystal Structure.

The crystal structure of solid chlorine has been shown by X-ray analysis to be tetragonal with $c/a = 0{\cdot}715$. The unit cell has $a = 8{\cdot}56$ A., $c = 6{\cdot}12$ A., the space-group being D_4^{1h}. The (x,y,z) co-ordinates of the Cl atom are (0·125, 0·167, 0·107) [29] These results are in conflict with the older work (Mellor, II, 47), in which the crystals were reported to be rhombic.

Viscosity.

Braune and Linke determined the viscosity of gaseous chlorine by observing the damping of torsional oscillations of a thin quartz disc suspended in the gas (at 90 mm. pressure) between two other parallel discs, air being used to standardize the apparatus. Results were as follows:-

Temperature, °K.	288·8	498·7	570·2	580·5	606·6
Viscosity ($\times 10^7$), poise	1294	2191	2480	2539	2626
Temperature, °K.	675·9	692·7	747·5	772·0	
Viscosity ($\times 10^7$), poise	2870	2948	3143	3209	

The constant C in Sutherland's equation,

$$\eta \text{ (viscosity)} = \frac{KT^{1/2}}{C+T}$$

was found to have the value 351 ($K = 168{\cdot}2 \times 10^{-7}$). A value of 3·72 A. for the collision diameter of the chlorine molecule was derived from these results.[30]

Trautz and his collaborators measured the viscosity of the gas by a transpiration method, i.e. the gas was discharged for a measured time from a reservoir, of known volume, through a capillary tube maintained at any desired temperature, and the fall of pressure in the reservoir was recorded. The apparatus was calibrated with both air and sulphur dioxide. Values reproducible to ±0·2% were obtained, as follows:-

Temperature, °K.	293·1	328·2	372·5	418·5	472·6	523·0
$\eta \times 10^7$, poise	1312	1470	1651	1845	2081	2244

The values found for Sutherland's constant (C) and the temperature index (n) were:-

Temperature Range, °C.	20–100	100–150	150–200	200–250
C	279	327	474	433
n	0·958	0·953	0·989	0·956

In a later paper, the values of η were recalculated and adjusted to even multiples of °C., and new values were reported from determinations with improved apparatus and more carefully purified gas. The results are given in Table V.

TABLE V. - VISCOSITY OF GASEOUS CHLORINE

Temperature, °C.	20	50	100	150	200	250
$\eta \times 10^7$ (previous values recalculated)	1288	1428	1639	1854	2073	2244
$\eta \times 10^7$ (new values)	1327	1469	1679	1875	2085	2276

The value calculated for the collision molecular diameter was 5·88 A., notably higher than the above value although the values of η are similar.[31,32]

More recent determinations[33] of the viscosity, made by the falling-ball method, gave $\eta = 1333 \times 10^{-7}$ poise at 20°C., the Sutherland constant being 345 over the range 20 – 100°, and the mean temperature index being 1·01.

Steacie and Johnson found that the viscosity of liquid chlorine, determined in an Ostwald viscometer, is expressible by the formula:

η_t (poise) $=\eta_0/(1+At+Bt^2)$, where $\eta_0=0{\cdot}00385$, $A=0{\cdot}005878$, $B=-0{\cdot}00000392$, and t is in °C. The values of η_t at −76·5° and −33·8° are respectively 0·00729 and 0·00488 poise.[34] The viscosity at the m.p. (−102°C.) has been estimated, by extrapolation from these results, to be 0·0104 poise.[35]

The 'rheochor', defined by the equation $R = M\eta^{1/8}\ (D + 2d)$, where M = molecular weight, η is in millipoises, and D and d are respectively the density of the liquid and the gas, has for liquid chlorine at the b.p. the value 2 × 27·7. The contribution to the rheochor of an organic compound, made by a chlorine atom in the molecule, is 27·3 units.[36]

Vapour Pressure of Liquid and Solid Chlorine.

Henglein and collaborators determined the vapour pressure by finding the weight of gas filling a vessel, of known volume, which was connected to a reservoir containing the liquid or solid at a known temperature. A vibrating quartz-fibre manometer was used for pressure measurements at 119° and 126°K. Their results were as follows:-

Temperature, °K.	119·2	126·0	133·0	146·6	161·1	} for the solid
p, mm.	0·0015	0·0067	∼0·03	0·26	2·64	

Temperature, °K.	170°(m.p.)	177·6	194·5	} for the liquid
p, mm.	8·9	17·40	64·40	

The values for the solid are expressible with fair accuracy by the equation $\log p_{\mathrm{mm.}} = -1530/T + 9{\cdot}950$, and those for the liquid by $\log p_{\mathrm{mm.}} = -1160/T + 7{\cdot}773$.[37]

Trautz and Gerwig, using both static and dynamic methods of measurement, found notably lower vapour pressures of the liquid over the range 194 − 238°K. These fitted an equation $\log p_{\mathrm{mm.}} = -(1085/T) + 7{\cdot}433$.[38]

Harteck used a quartz-spiral manometer and found the following values, among others, for the vapour pressure:[39]

Temperature, °K.	162·7	165·7	170·3	172·6*		(solid)
p, mm.	2·6	3·4	7·2	9·8		
Temperature, °K.	172·7	178·8	180·2	183·7	185·8	(liquid)
p, mm.	9·9	17·4	19·6	26·9	31·8	
Temperature, °K.	198·1	210·9	220·4	234·5	245·2	(liquid)
p, mm.	78·1	175·5	302·4	611	634	

* triple point (−100·5°C.)

Giauque and Powell, using a mercury manometer protected by a carbon dioxide buffer, obtained the following values for the vapour pressure of the liquid; their figures, which are a little higher than those of Harteck, have been rounded off:-

Temperature, °K.	172·12*	175·44	180·38	185·46	190·51
p, mm.	10·44	14·07	21·58	32·50	47·74
Temperature, °K.	195·51	200·41	205·24	210·00	215·18
p, mm.	68·31	95·07	129·49	172·74	232·5
Temperature, °K.	219·91	225·10	229·96	234·98	240·05
p, mm.	301·3	394·0	500·4	632·7	793·9

* triple point (−100·98°C.)

These values are expressible by the formula $\log p\ (\mathrm{mm.}) = -(1414{\cdot}8/T) - 0{\cdot}01206T + 1{\cdot}34 \times 10^{-5}T^2 + 9{\cdot}91635$. An accuracy of 0·1 − 0·2% was claimed for them.[40]

Ziegler[8] combined the results of Giauque and Powell with those found by

Pellaton for higher temperatures (Mellor, II, 52) to give the formula $\log\pi = -4{\cdot}06276 \log\theta + 0{\cdot}22341 (\theta^4 - 16/\theta + 15)$, where π and θ are respectively the vapour pressure and absolute temperature, reduced to fractions of the corresponding critical values. This formula was claimed to agree with the observed values within 1% over the range from −70° to the critical point, apart from isolated larger deviations due to the 'scatter' of Pellaton's results (the values taken for the critical temperature and pressure being respectively 144·0° and 76·0 atm.). The following is a selection of the vapour-pressure values tabulated in the original (here recalculated from the 'technical atmosphere' (at.) to the standard atmosphere (atm.)):[8]

Temperature, °C.	−75	−35	0	20	40	60	80
Vapour pressure, atm.	0·1493	0·995	3·64	6·64	11·15	18·11	26·2

Temperature, °C.	100	120	140	144 (critical)
Vapour pressure, atm.	37·6	52·5	71·6	76·0

On the same basis Hulme and Tillman tabulated the vapour pressure in lb. per sq.in. at 5° or 10°F. intervals from −50° to +291·2°F. The formula used was: $\log P = -1901{\cdot}988/T - 6{\cdot}95 \times 10^{-2} \log T + 5{\cdot}78109$, T being in °Rankine (i.e., °F. absolute).[9]

Boiling Point.

Recent determinations of the normal b.p. of chlorine have given the following closely concordant values:-

Investigators	Date	Boiling Point °C. at 760 mm.
Trautz & Gerwig[38]	1924	−34·7
Harteck[39]	1928	−33·95 ± 0·10
Giauque & Powell[40]	1939	−34·05
Ziegler*[8]	1950	−34·15

* Estimate based on results of earlier workers.

Melting Point.

Values recorded for the m.p. of chlorine are:-

Investigators	Date	Melting Point, °C.
Maass & Boomer[41]	1922	−100·3
Henglein et al.[37]	1922	−103
Eucken & Karwat[42]	1924	−102·3
Harteck[39]	1928	−100·5
Graff[43]	1933	−103 ± 0·3
Wheat & Browne[44]	1936	−102·0
Giauque & Powell[40]	1939	−100·98

The last result, which is probably the most accurate, differs by only 1° from Olschewsky's value, −102° (Mellor, II, 53).

Critical Constants.

Values given for the critical constants of chlorine are:-

Authority	Date	t_c °C.	P_c atm.	V_c c.c./g.	d_c g./c.c.
Pickering[45]	1924	143·9	76	1·745	0·573
Ziegler[8]	1950	144·0	76·0	1·763	0·5672
Hulme & Tillman[9]	1949	291·2°F.	1154(lb./sq.in.)	0·0279(cu.ft./lb.)	

All these data are based on reviews of earlier work (Mellor, II, 52).

Internal Pressure.

The internal pressure of liquid chlorine at the b.p. has been calculated as 2169 atm., from an equation involving the critical temperature, the b.p. and the molecular volume.[46] Another author, using five different semi-empirical relations, obtained values ranging from 2074 to 4416 atm., at 25°C. (the value 2074, given here, corrects a numerical error in the original paper).[47]

Parachor.

Sugden calculated for the parachor of chlorine the value 111·5.[48] Values given for the atomic contribution of chlorine to the parachors of organic compounds are respectively 54·3,[48] 55·0,[49] 54·6,[50] 55·2[51] and 55[52] units.

Optical Properties.

Values given for the atomic refraction of chlorine (combined in organic compounds) are $R_D = 5{\cdot}74-6{\cdot}01$,[53] and $R_C = 5{\cdot}821$, $R_D = 5{\cdot}844$, $R_F = 5{\cdot}918$, $R_{G'} = 5{\cdot}973$.[51] The refractivity of the chlorine ion (Cl^-) has been found to be 9·30 for infinitely long waves (in the gas phase),[54] or $9{\cdot}06_5$ for the D line (taking $R_{Na^+} = 0{\cdot}200$; with $R_{Na^+} = 0{\cdot}350$, the value becomes 8·91).[55] For the Cl^- ion in solution, the refractivity for the D line is reported to be 9·06[56] or $9{\cdot}03_2$.[57]

The emission and absorption spectra of chlorine, and molecular constants derived therefrom, are dealt with in the section on spectroscopy (see page 621), and the optical dissociation of chlorine is referred to also in the account of the hydrogen–chlorine photochemical reaction. Here it will suffice to mention that neither the intensity of absorption, nor the convergence limit 4786 A. (below which light-absorption causes dissociation) is found to be affected by the presence of moisture or of a moderate pressure of air.[58-61]

It is also very doubtful whether the moisture content of the gas has an influence on the expansion under illumination (Budde effect; see Mellor, II, 63).[58,60,62]

An attempt to detect a change of refractive index on irradiation of chlorine gave a negative result,[63] but it has been reported that a slight increase in diamagnetic susceptibility occurs.[64]

Cole found that the depolarization factor in the scattering of light by chlorine which contained 2% carbon dioxide was 4·1% for the gas and 24% for the liquid; these values were unaffected by prolonged drying over phosphorus pentoxide. The intensity of the scattered light in the gas and liquid was respectively 0·99 and 1·77 times that observed with ether in the same respective states.[65] Other workers found values of 4·07% and 4·37% respectively for the depolarization factor with the gas.[66,67]

Velocity of Supersonic Waves in Chlorine.

Some of the values obtained by Eucken and Becker[68] are given in Table VI.

TABLE VI. - VELOCITY OF SUPERSONIC WAVES IN CHLORINE

Temperature °C.	Pressure mm.	Frequency kcs.	Velocity m./sec.
–32·7	746	58·4	194·4
+18·0	744	58·4	215·0
74·0	755	58·4	233·6
142·5	749	58·4	253·6
18·1	750	145·8	217·2
17·9	754	292	216·8

These results are discussed in connexion with the heat capacity (see page 336).

They are in agreement with later work by Schultze, who further found for the velocity of audible sound waves (3 kcs.) values of 194·95 and 204·82 m./sec., respectively at −25° and 0°C.[86]

Adsorption Phenomena with Chlorine.

Chlorine is strongly adsorbed by active charcoal; e.g. Remy and Hene found 234 c.c. (= 0·70 g.) of chlorine to be adsorbed per g. of charcoal at 15°C./1 atm., and Reyerson and Wishart found that a specimen of charcoal adsorbed 0·3997 g./g. at 35·5°/673 mm., or 0·359 g./g. at 91·5°/722 mm.[69] Isotherms both of the Langmuir and of the Freundlich type have been reported.[69-71] When charcoal has adsorbed chlorine, part of the adsorbate is very difficult to remove, whether by strong heating, or evacuation, or treatment with alkali: this has been attributed to substitutive reaction with combined hydrogen atoms in the impurities in the charcoal.[72-75]

The adsorptive capacity of charcoal for other substances is liable to be reduced by previous adsorption and desorption of chlorine:[73] Fig. 1, taken from the work of Emmett, illustrates this point.[75]

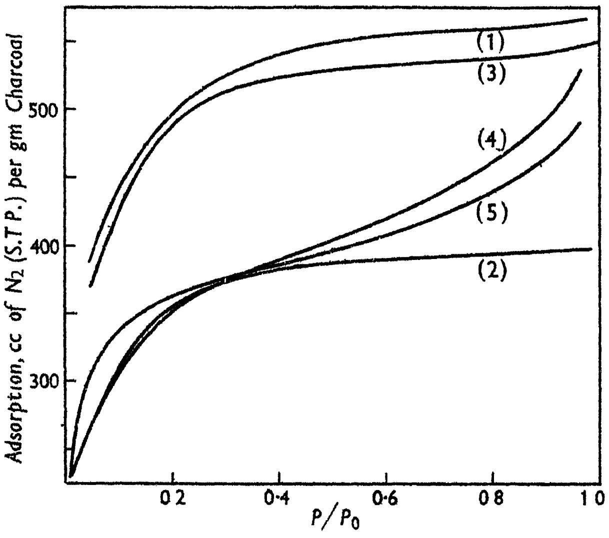

Fig. 1. Adsorption of nitrogen at −195°C. as a function of treatment of the charcoal with chlorine. (1) Untreated; (2) after chlorine adsorption at 200°C. and evacuation at room temperature; (3) after evacuation at 100°C.; and (4) and (5) after evacuation at 200°C.

On the other hand, it has been reported that exposure of charcoal to chlorine, followed by heating to redness in vacuo, increased its adsorptive capacity,[76] and a similar effect was found by treating vegetable charcoal with chlorine at 750 – 950°C.[74]

Equilibrium in chlorine adsorption on charcoal is established rather slowly; hence it has been supposed that the adsorption is of the activated type, or that adsorption is followed by absorption.[69,70]

Reyerson and Wishart gave 8·86 kg.-cal./mole for the 'differential' heat of adsorption of chlorine on charcoal, i.e. about twice the heat of evaporation at 20°C.[69] The heat of adsorption in the initial stages may be at the rate of

31 kg.-cal./mole of Cl_2, declining as the proportion of adsorbed chlorine increases.[77] It has been reported that the heat of adsorption of chlorine on charcoal is 146% more than that on silica gel[73] (but see below).

Bohart and Adams found that when charcoal was used, as in a gas-mask, to adsorb chlorine from a gas stream, the break-point time was at a minimum for 50% relative humidity of the gas,[76] but Nielsen found that a small amount of moisture lengthened the break-point time.[78] Rather complex effects are obtained, in this application, when varying percentages of water are initially present on the charcoal, but in general the break-point time is not greatly affected. Moisture much increases the break-point time when the charcoal has been activated with zinc chloride. Owing to hydrolysis ($2Cl_2 + 2H_2O \rightleftharpoons 4HCl + O_2$), with moisture present the first toxic gas to break through the charcoal is usually hydrogen chloride, with a chlorine/hydrogen chloride mixture following later.[78,79]

The adsorptive capacity of charcoal for chlorine is increased by impregnation with alkali hydroxide or carbonate, especially in presence of moisture; this is presumably a chemical effect.[80,81]

Chlorine is also rather strongly adsorbed by silica gel. The results of Magnus and Müller, for example, show the adsorption of 0·1637 g. chlorine/g. gel at 0°C./474 mm. or 0·0703 g./g. at 40°/677 mm.[83] The isotherms are of the Freundlich type, although in the initial stages Henry's law applies.[82,83] From measurements in the region −25° to +30°, Reyerson and Bemmels obtained straight lines by plotting $P/[V(P_0-P)]$ against P/P_0, where V is the volume sorbed, P is the pressure of the vapour, and P_0 is the saturation pressure of the liquid at the prevailing temperature; these results are in accord with Brunauer's multilayer adsorption theory.[84] Magnus and Müller determined the 'differential' heat of adsorption by application of the Clapeyron-Clausius equation to pairs of isotherms, and found e.g. at 20°C. that the value was 7·00 kg.-cal./mole Cl_2 with 0·026 mole chlorine adsorbed per g. gel, and 5·91 kg.-cal./mole with 1 m.-mole/g.[83]

The adsorption of chlorine by porous magnesium oxide, in the range 25 – 45°C./20 – 700 mm., follows Freundlich's equation.[85]

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THERMODYNAMIC PROPERTIES

Heat of Vaporization.

From vapour pressure measurements at various low temperatures, the following estimates of the heat of sublimation of solid chlorine have been made:-

Investigators	Date	Heat of Sublimation g.-cal./mole.
Henglein et al.[1]	1922	6960 at m.p.(–103°)
Eucken et al.[2]	1924	7220 at 0°K.
Harteck[3]	1928	7370 ± 10 at 0°K.

According to Kelley[4] the heat of sublimation at any temperature is given approximately by the expression $7430 - 5{\cdot}0\,T$ g.-cal./mole. (T in °K.).

From his theory of molecular forces (see page 325) London[5] calculated that the lattice energy of solid chlorine, i.e. the heat of sublimation at 0°K. minus the zero-point energy, is 7180 g.-cal./mole, and compared this value with an experimental value of 7430 g.-cal./mole.

Determinations[6] of the ebullioscopic constant for solutions of chloroform, carbon tetrachloride, and stannic chloride in liquid chlorine gave a value of 1·73, corresponding to 66·0 g.-cal./g., or 4680 g.-cal./mole. for the heat of vaporization of the liquid at its b.p.

Vapour pressure measurements of the liquid have yielded the following values for its heat of evaporation:-

Investigators	Date	Heat of Evaporation g.-cal./mole.
Henglein et al.[1]	1922	5300 at f.p. (–103°C.)
Trautz & Gerwig[7]	1924	4962 between –79° and –34·8°C.
Wohl[8]	1924	5450 } revision of preceding 5350 } figures, respectively
Giauque & Powell[9]	1939	4878 ± 4 at b.p. (–34·05°C.)

Kelley[4] gives the expression $6330 - 8{\cdot}0\,T$ g.-cal./mole (T in °K.) as an approximation for the heat of evaporation at any temperature, but this is obviously in error near the critical temperature, 417°K.

Ziegler,[10] by means of a formula based on the Clapeyron-Clausius equation, has tabulated the heat of evaporation for every 5° from –70°C. up to the critical temperature. A selection of his values is given in Table VII.

TABLE VII. - HEAT OF EVAPORATION OF CHLORINE

Temperature, °C.	–70	–35	0	20	40	
Heat of Evaporation, g.-cal./g.	73·30	68·75	63·60	60·38	56·92	
Temperature, °C.	60	80	100	120	140	144
Heat of Evaporation, g.-cal./g.	53·04	48·39	42·24	33·34	17·0	0

These values agree well with the experimental data (see above and Mellor, II, 54), which, however, are available only for the lower part of the temperature range considered.

Hulme and Tillman[11] have given a table of values of the heat of evaporation, expressed in B. Th. U./lb., from –60°F. up to the critical point. Though derived by a different method (that of Gordon[30]), their results agree closely with those of Ziegler.

Heat of Fusion.

Values for the heat of fusion of chlorine are given below: the last value is probably to be preferred.

Investigators	Date	Heat of fusion g.-cal./mole
Henglein et al.[1]	1922	1660
Eucken & Karwat[12]	1924	1615
Giauque & Powell[9]	1939	1531

Heat Capacity.

The recent literature concerning the heat capacity of gaseous chlorine is extensive. By measurement of the temperatures attained on explosion of hydrogen–chlorine mixtures containing an excess of chlorine, Wohl[13] found that the mean heat capacity of (undissociated) chlorine gas, at constant volume between 291 and 1335°K., is 6·83 ± 1·3% g.-cal./mole. He stated that the mean value between 291° and other temperatures is expressible by the formula $4{\cdot}963 + \frac{E_T - E_{291}}{T - 291}$ g.-cal./mole, where E is an Einstein function with 2·2 degrees of freedom ($E_{291} = 93$). A revision of this work gave the mean values of C_v between 291° and various temperatures as follows:[14]

Temperature, °K.	1651	1868	2054
Mean C_v, g.-cal./mole.	6·886	6·914	6·935

By an adiabatic expansion method, Eucken and Hoffmann found the following values for C_p, the heat capacity (g.-cal./mole) at constant pressure at particular temperatures. They also checked their results by calculations from spectroscopic data:[15]

Temperature, °K.	203·3	270·2	318·4	391·4	451·7
C_p, calc. to 1 atm.	8·279	8·280	8·285	8·499	8·558
C_p, calc. to zero pressure	7·790	7·927	8·095	8·409	8·503
C_p, calc. from spectroscopic data	7·798	7·935	8·138	8·357	8·481

Nernst & Wohl likewise used spectroscopic data to derive values for C_v of 5·97 g.-cal./mole at 273°K. and 6·32 at 373°, rising gradually to 7·0 at 2000° and 2800°. (The corresponding values of C_p are respectively 7·96, 8·31 and 9·0 g.-cal./mole).[16]

In measurements of the velocity of ultrasonic waves in chlorine, Eucken and Becker found that the ratio C_p/C_v at 18°C. rose from about 1·33 to 1·40 as the wave frequency was raised from low values up to 292 kc., showing that at the higher frequencies the adiabatic temperature changes were too rapid for equilibrium to be set up between translational and vibrational motion; the heat capacity therefore diminishes. (It was calculated that, at 18°, 34000 collisions are required on the average for the molecule to acquire a quantum of vibrational energy). The effect becomes evident at lower frequencies if the temperature is low. It sets in only at very high frequencies if the chlorine contains small amounts of foreign gases, in particular hydrogen chloride.[17]

Schulze confirmed Eucken and Becker's work and showed that at −25°C. the effect is detectable at 3 kcs. His estimates for the 'relaxation' time were $3{\cdot}9 \times 10^{-6}$ sec. at 0° and $7{\cdot}6 \times 10^{-6}$ sec. at −25°. His results yielded the following values of C_v (at low frequency):[18]

Temperature, °C.	−25	0	18	32
C_v, g.-cal./mole	5·839	5·987	6·068	6·109

A number of later workers have derived the heat capacity by applying statistical mechanics to the careful analyses of the rotational and vibrational terms of the chlorine spectrum made by Elliott[19] and by Herzberg.[20] This procedure probably gives more accurate results than any experimental method.

A selection of Trautz and Ader's[21] values for C_v, obtained in this way, is (for the normal isotopic mixture):-

Temperature, °K.	100	200	273·1	373	673	1073	2000
C_v, g.-cal./mole.	5·0119	5·5890	6·0016	6·3660	6·7839	6·9548	7·0583

These values correspond to values of C_p up to 1·3% higher than those of Eucken and Hoffmann, and are up to 1·4% higher than those of Nernst and Wohl.

Data from the most recent table of values for C_p, calculated in the same way and again taking account of isotopes, are:[22]

Temperature, °K.	200	273·16	298·16	300	400	500	600
C_p, g.-cal./mole (1 atm.)	7·576	7·999	8·112	8·119	8·438	8·624	8·742

Temperature, °K.	700	800	900	1000	1200	1600	2000
C_p, g.-cal./mole (1 atm.)	8·822	8·880	8·924	8·960	9·015	9·096	9·159

These values are almost identical with those tabulated by the U.S. National Bureau of Standards.[23] They are stated to be expressible by the equation $C_p = 6{\cdot}860 + 4{\cdot}994 \times 10^{-3}\,T - 3{\cdot}745 \times 10^{-6}\,T^2 + 0{\cdot}9214 \times 10^{-9}\,T^3$ (average deviation 0·65%, maximum 1·85%).[22]

The following is a selection from a table of the mean values of C_p between 0°C. and various temperatures:-

Temperature, °C.	0	100	400	800	1200
Mean C_p, g.-cal./mole (1 atm.)	7·99	8·20	8·53	8·72	8·82

These data correspond to the same values of C_p as in the preceding table, but the authors give a slightly different algebraic expression for C_p, viz. $C_p = 6{\cdot}8214 + 5{\cdot}7095 \times 10^{-3}\,T - 5{\cdot}107 \times 10^{-6}T^2 + 15{\cdot}47 \times 10^{-10}\,T^3$ (average deviation 0·23%, maximum 0·50%, over the range 273 – 1500°K.).[24]

Another algebraic expression, claimed[25] to give the spectroscopically derived heat capacity still more closely than the preceding, is C_p (for ideal gas) $= 8{\cdot}911 + 0{\cdot}140 \times 10^{-3}\,T - 0{\cdot}0298 \times 10^5/T^2$ (average deviation 0·02%, maximum 0·09%).[25] This superseded an earlier expression,[26] $C_p = 7{\cdot}5755 + 2{\cdot}4244 \times 10^{-3}\,T - 9{\cdot}650 \times 10^{-7}\,T^2$ (average deviation 0·59%). Kelley claimed that a modification of the former equation, *viz.*, C_p (ideal gas) $= 8{\cdot}82 + 0{\cdot}06 \times 10^{-3}\,T - 0{\cdot}68 \times 10^5/T^2$, g.-cal./mole, enables enthalpies to be calculated which are accurate to 1% over the range 298 – 3000°K.[27]

Simpler expressions, less accurate except perhaps at lower temperatures, have been given as follows:-

Author	Temperature range °K.	C_p g.-cal./mole.	Accuracy claimed %
Eastman[28]	300 – 700	$5{\cdot}88 + 9{\cdot}35 \times 10^{-3}\,T - 7{\cdot}00 \times 10^{-6}\,T^2$	2·5
Eastman[28]	300 – 2500	$8{\cdot}58 + 0{\cdot}30 \times 10^{-3}\,T$	5
Kelley[29]	273 – 2000	$8{\cdot}28 + 0{\cdot}56 \times 10^{-3}\,T$	1·5

Also Ziegler gave for the heat capacity at zero pressure, in g.-cal./g., the expression $0{\cdot}11210 + 0{\cdot}66094 \times 10^{-4}\,t - 0{\cdot}14468 \times 10^{-6}\,t^2$($t$ in °C.); in the range −73° to + 200°C., the maximum deviation from the spectroscopic values is 0·58%.[10]

The heat capacity of solid and liquid chlorine has been determined[11] down to 21·9°K. A selection of the results for the solid is as follows:-

Temperature, °K.	10	20	30	40	60	80	100
C_p, g.-cal./mole	0·34*	1·88*	4·16	6·20	8·52	9·55	10·35

Temperature, °K.	130	160	170·5
C_p, g.-cal./mole	11·67	13·38	14·00

(* estimated.)

For the liquid a constant value, 16·25 g.-cal./mole, was found over the range 170·8 – 230°K. The accuracy claimed was 2% for the solid and 3% for the liquid.

Rather lower values were obtained by Giauque and Powell, e.g.:-

Temperature, °K.	15	20	50	70	100	120	150
C_p, g.-cal./mole	0·89	1·85	6·99	8·68	10·10	10·87	12·20

Temperature, °K.	170	172·12	172·12	200	220	240
C_p, g.-cal./mole	13·17	13·27	16·03	15·95	15·84	15·70
		(solid)	(liquid)			

The accuracy claimed[9] was 0·1 – 0·2% above 25°K., 1% at 20°, and several percent. below 20°.

Recent determinations of the heat capacity of the liquid above its normal b.p. are lacking. Ziegler calculated values up to 125°C. by means of an equation:-

$$c' = \frac{d(h' - h_0')}{dT} - Av'\frac{dP}{dT},$$

where c' is the heat capacity, $h' - h_0'$ is the enthalpy referred to 0°C., A is the gas constant and v' is the specific volume (all referred to 1 kg. of liquid). Up to 40° the value of c' is almost constant at 0·23 kg.-cal./kg., but rises gradually to 0·25 at 75° and more steeply to 0·40 at 115°.[10]

Enthalpy (Heat Content).

The enthalpy of chlorine gas at 1 atm. has been calculated, by integration of spectroscopic heat-capacity values over the appropriate ranges of temperature, to have the values shown in Table VIII, where H_0° is the enthalpy the ideal gas would have if it existed at 0°K. and 1 atm.:-

TABLE VIII. - ENTHALPY OF CHLORINE GAS AT 1 atm.

Authors:	Kelley[27]	Kobe & Long[24]	Arnold & Kobe[22]
Temp. °K.	$H_T^\circ - H_{298.16}^\circ$ g.-cal./mole	$H_T^\circ - H_{273}^\circ$ g.-cal./mole	$\frac{H_T^\circ - H_0^\circ}{T}$ $\frac{\text{g.-cal.}}{\text{deg. mole}}$
200	–	–	7·108
273·16	–	0	7·293
291	–	144·6	–
298·16	0	201·3	7·357
300	–	214·9	7·362
400	840	1044	7·594
600	2544	2766	7·934
800	4296	4530	8·155
1000	6059	6314	8·309
1200	7830	8112	8·422
1500	–	10827	–
1600	11385	–	8·581
2000	14950	–	8·690
2500	19405	–	–
3000	23870	–	–

Kelley gave an equation $H_T^\circ - H_{298\cdot16}^\circ = 8\cdot82\,T + 0\cdot03 \times 10^{-3}T^2 + 0\cdot68 \times 10^5\,T^{-1} - 2861$,, which fits his values within 1%. His values are seen to agree closely with those of Kobe and Long, if 201·3 is added for $H_{298\cdot16}^0 - H_{273.16}^0$.

A selection from a table of values calculated by Hulme[31] for the enthalpy, in B.Th.U./lb., of the (superheated) gas at various pressures and temperatures is given in Table IX.

TABLE IX. - ENTHALPY OF CHLORINE GAS AT VARIOUS PRESSURES AND TEMPERATURES

Pressure lb.per sq.in.	Temperature, °F.					
	0	50	100	200	300	400
10	230·76	236·90	243·03	255·29	267·49	279·72
30	—	236·11	242·25	254·69	267·13	279·56
50	—	235·31	241·45	254·10	266·75	279·40
80	—	—	240·30	253·25	266·20	279·16
120	—	—	239·03	252·26	265·49	278·72
200	—	—	—	250·25	264·20	277·63
300	—	—	—	246·58	262·00	276·00
400	—	—	—	242·80	259·70	274·24

The consistency of these data with thermodynamic principles has, however, been called in question.[32]

The enthalpy of the saturated vapour was calculated by Ziegler from a complex expression derived from his equation of state and his formula for the heat of capacity (see page 338). Corresponding values for the enthalpy of the boiling liquid were obtained by deducting the heats of evaporation (see page 335). The following are some of his results (enthalpy of the liquid at 0°C. arbitrarily taken as 100 g.-cal./g.):-

Temperature, °C.	−70	−35	0	20	40	60
Enthalpy of liquid, g.-cal./g.	83·86	91·85	100	104·66	109·31	114·05
Enthalpy of saturated vapour, g.-cal./g.	157·16	160·60	163·60	165·04	166·23	167·09

Temperature, °C.	80	100	120	140	144 (critical)
Enthalpy of liquid, g.-cal./g.	119·08	125·00	132·47	144·2	153·41
Enthalpy of saturated vapour, g.-cal./g.	167·47	167·24	165·81	161·2	153·41

These results were plotted on a Mollier diagram (enthalpy against logarithm of vapour pressure). The diagram includes also isochores, isotherms and isentropic lines which are continued into the region of superheat.[10]

A table is also available of enthalpy values for the boiling liquid and saturated vapour, expressed in B.Th.U./lb., together with a Mollier diagram in which enthalpy is plotted against temperature. Although in the calculation of the enthalpies a rather inadequate expression was used for the heat capacity of the vapour, the divergence from Ziegler's values is slight except at the higher temperatures.[11]

Eucken and Karwat[12] obtained the following values for the enthalpy of *solid* chlorine (and of the liquid below its normal boiling-point) by integration of their heat-capacity data (see page 336):-

Temperature, °K.	10	20	30	40	60	80	100
$H_T^\circ - H_0^\circ$ g.-cal./mole	0·87	11·40	41·70	93·66	244·5	426	625

Temperature, °K.	130	160	170·5	170·8	180	200	230
$H_T^\circ - H_0^\circ$ g.-cal./mole	956	1331	1480	3091	3240	3565	4052
			solid	liquid			

These figures may be somewhat in error, in view of the divergence between the authors' heat capacity values and those of Giauque and Powell.

Entropy.

An early estimate of the 'absolute' entropy of gaseous chlorine at 298°K., based on electrode-potential measurements, was 54·2 g.-cal./deg. mole. Inaccurate heat-capacity data were utilized.[33] A revised calculation on the same basis gave $S_{298\cdot1}$ = 53.0 ± 0·4 g.-cal./deg. mole.[34]

Other earlier workers estimated the entropy of crystalline chlorine at absolute zero by consideration of 'chemical constants' derived from vapour-pressure equations and from hydrogen-reduction equilibria. The values obtained[35,36] were respectively $R \ln 2$ (= 1·37) and 7·6 + 0·95 ($\log 2n_2 - 1$), where n_2 represents the value of the nuclear spin of ^{37}Cl.

More recent calculations of the entropy have been based on the spectroscopically derived heat capacity of the gas, and on the accurate thermal data now available for the liquid and solid. In this way Giauque and Overstreet derived the following values for the various isotopic forms of the gas at 25°C. (298·1°K.):-

Isotope	$^{35}Cl-^{35}Cl$	$^{35}Cl-^{37}Cl$	$^{37}Cl-^{37}Cl$	Usual Mixture
Entropy, g.-cal./deg.mole	53·235	53·389	53·543	53·310

These values do not include contributions due to nuclear spin or isotopic mixing. The same authors calculated an entropy of 53·38 g.-cal./deg.mole from e.m.f. measurements of Eastman and Milner.[37,38]

Giauque and Powell gave the following entropy values, based on their heat-capacity determinations and the third law of thermodynamics:-

	g.-cal./deg.mole
Solid at m.p. (172·12°K.)	16·904
Liquid at m.p. (172·12°K.)	25·799
Liquid at normal b.p. (240·05°K.)	31·030
Gas (actual) at normal b.p. (240·05°K.)	51·44
Gas (ideal) at normal b.p. (240·05°K.)	51·56
Gas (ideal) at 298·1°K.	53·32

The last two figures agree very closely with the values derived from spectroscopic data, 51·55 and 53·31 g.-cal./deg.mole respectively. As before, the entropy due to isotopic mixing and nuclear spin is not included.[9] In an earlier calculation by the above method, but using older thermal data, Kelley had obtained $S_{298\cdot1}$ = 53·0 ± 0·4 g.-cal./deg.mole.[34]

Table X gives a selection from recently calculated values for the entropy of the gas at various temperatures,[22] the symbol ° referring here, as elsewhere, to the ideal gas at 1 atm. pressure. (see page 341).

These values agree closely with those in the U.S. Bureau of Standards tables[23] and with values of $S_T^\circ - S_{298\cdot16}^\circ$ tabulated by Kelley.[27]

Hulme calculated values for the entropy of the gas at various temperatures and pressures; a selection is given in Table XI. The entropy in g.-cal./mole °C. may be derived from the above by multiplying by 70·914. As already mentioned, the soundness of Hulme's calculations has been questioned, but

TABLE X. - ENTROPY OF CHLORINE GAS AT VARIOUS TEMPERATURES

Temp. °K.	S° g.-cal./deg.mole	Temp. °K.	S° g.-cal./deg.mole	Temp. °K.	S° g.-cal./deg.mole
200	50·158	500	57·629	1000	63·740
273·16	52·586	600	59·213	1200	65·378
298·16	53·291	700	60·567	1400	66·771
300	53·341	800	61·749	1600	67·983
400	55·724	900	62·797	2000	70·019

TABLE XI. - ENTROPY OF CHLORINE GAS AT VARIOUS PRESSURES, EXPRESSED IN B.Th.U./lb.°F.

Pressure lb./sq.in.	Temperature, °F.					
	0	50	100	200	300	400
10	0·7456	0·7574	0·7680	0·7859	0·8026	0·8165
30	—	0·7258	0·7364	0·7544	0·7712	0·7851
50	—	0·7104	0·7210	0·7394	0·7569	0·7708
80	—	—	0·7061	0·7244	0·7421	0·7577
120	—	—	0·6931	0·7118	0·7302	0·7464
200	—	—	—	0·6943	0·7141	0·7319
300	—	—	—	0·6784	0·6992	0·7200
400	—	—	—	0·6670	0·6902	0·7112

Hulme maintains that more accurate values cannot be obtained in default of accurate experimental determination of P–V–T relations for chlorine in the range considered.[31,32]

The entropy of the saturated vapour was calculated by Ziegler on a similar basis to his calculation of the enthalpy (see page 339), and the corresponding entropy of the boiling liquid was obtained by deducting the entropy of vaporization. A selection of his results is given below (entropy of the liquid at 0°C. arbitrarily set at 1·0000 g.-cal./g. °C.):-

Temperature, °C.	−70	−35	0	20	40	60
Entropy of Liquid g.-cal./g. °C.	0·9320	0·9683	1·0000	1·0162	1·0314	1·0457
Entropy of Satd. Vapour g.-cal./g. °C.	1·2928	1·2569	1·2328	1·2222	1·2131	1·2049

Temperature, °C.	80	100	120	140	144 (critical)
Entropy of Liquid g.-cal./g. °C.	1·0599	1·0749	1·0936	1·1210	1·1432
Entropy of Satd. Vapour g.-cal./g. °C.	1·1969	1·1881	1·1784	1·1622	1·1432

These values were embodied in the Mollier diagram already referred to.[10] A table of similar values expressed in B.Th.U./lb. °F., is also available.[31]

Free Energy.

The free-energy function of gaseous chlorine was calculated by Giauque and Overstreet with the aid of spectroscopic data and the equation $\frac{G^\circ - E^\circ_0}{T} = -\tfrac{3}{2}R\ln M - \tfrac{5}{2}R\ln T + R\ln P - C - R\ln R - R\ln Q$ (here E°_0 is the internal energy at 0°K., M the mol. wt., T is in °K., P in atm., $R = 1{\cdot}9869$, $C + R\ln R = -7{\cdot}267$, and Q is the sum of the partition functions for all energy levels contributing appreciably to the heat capacity at temperature T). The following is a selection of the values found for the normal equilibrium mixture of isotopes:

Temperature, °K.	250	300	500	700	1000
$-\frac{G^0-E^0_0}{T}$, g.-cal./deg.mole	45·951	45·997	49·865	52·531	55·453

Temperature, °K.	1500	2000	2500	3000
$-\frac{G^0-E^0_0}{T}$, g.-cal./deg.mole	58·876	61·363	63·324	64·956

The free-energy functions of $^{35}Cl-{}^{37}Cl$ and $^{37}Cl-{}^{37}Cl$ were calculated to have values, respectively, 0·14 – 0·16 and 0·28 – 0·32 g.-cal./deg.mole higher than that of $^{35}Cl-{}^{35}Cl$ over the range considered.[37]

Two other, more recent, tables of the free-energy function give values very slightly lower than the above.[22,23]

Chemical Constant.

The 'chemical constant' of molecular chlorine, i.e. the integration constant in the equation derived from the Nernst Heat Theorem to express the vapour pressure of the solid:-

$$\ln p' = -\frac{L}{RT} + \int_0^T \frac{dT}{RT^2}\int_0^T \Delta C'_p\, dT + i$$

(where $\Delta C'_p$ is the difference between the heat capacities of the vapour and the solid) has been estimated to have the following values:-

Authors	Date	Chemical Constant	Derived from
Henglein et al[1]	1922	–0·05 to +0·06	Thermal dissociation and v.p.
Henglein[39]	1922	0·02	
Eucken et al.[2]	1924	1·51 ± 0·16	V.p. of solid
Cox[40a]	1923	0·42 to 0·91	Dissociation and v.p.
Cox[40b]	1925	0·64	Dissociation
Wohl[6]	1924	1·96 ± 0·26	E.m.f. of aqueous heavy-metal cells
Jellinek & Uloth[41]	1926	2·06	H_2-reduction equilibrium of heavy-metal salts
Jellinek & Uloth[41]	1926	1·72	E.m.f. of fused-salt cells
Jellinek & Uloth[41]	1926	1·99 ± 0·18	(Mean of various methods)
v. Wisniewski[42]	1927	1·40	Theoretical model
Harteck[3]	1928	1·55 to 1·74	V.p.
Jellinek & Rudat[43]	1929	2·06	H_2-reduction equilibrium of $PbCl_2$
Stern[36]	1931	1·351	Calcd. v.p. of solid
Trautz & Ader[44]	1934	1·354	Spectroscopic data

The divergence between these estimates shows the limited usefulness of this application of the Heat Theorem.

Thermodynamic Properties of Monatomic Chlorine.

The thermodynamic properties of gaseous chlorine in the monatomic state are for the most part not open to experimental measurement, but they are accurately calculable from spectroscopic data of the chlorine atom. The following are some of the values given by Trautz & Ader for the heat capacity at constant volume:-

Temperature, °K.	129·86	259·72	324·65	432·76	541·08
C_v, g.-cal./ g.-atom.	2·9845	3·1462	3·2658	3·4039	3·4550

Temperature, °K.	574·41	618·38	865·73	1623·25	3246·5
C_v, g.-cal./ g.-atom.	3·4585(max.)	3·4563	3·3836	3·1704	3·0397

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The slow rise to a maximum value, followed by a decline towards the low-temperature value of $\frac{3}{2}R$, is due to excitation of the atoms to the $^2P_{1/2}$ state.[21]

The free-energy function was calculated by Giauque & Overstreet to have the following values (g.-cal./deg.g.-atom); the effect of isotopic mixing and nuclear spin was ignored:-[37]

Temperature, °K.	250	298·1	300	400	600	800
$-\dfrac{G^\circ-E^\circ_0}{T}$	33·555	34·437	34·468	35·924	38·015	39·521

Temperature, °K.	1000	1500	2000	3000
$-\dfrac{G^\circ-E^\circ_0}{T}$	40·687	42·836	44·346	46·456

A selection from the U.S. Bureau of Standards tables[23] for the heat-capacity at constant pressure, enthalpy function, entropy and free-energy function is given in Table XII ($H^\circ_0 \equiv E^\circ_0$):-

TABLE XII. - VALUES OF C_p, ENTHALPY FUNCTION, ENTROPY AND FREE-ENERGY FUNCTION FOR MONATOMIC CHLORINE

Temp. °K.	C_p g.-cal./ g.-atom	$(H^\circ-H^\circ_0)/T$ g.-cal./ deg.g.-atom	S° g.-cal./ deg.g.-atom	$(G^\circ-H^\circ_0)/T$ g.-cal./ deg.g.-atom
298·16	5·2203	5·0278	39·4569	−34·4291
300	5·2237	5·0290	39·4890	−34·4600
400	5·3705	5·0977	41·0138	−35·9161
500	5·4363	5·1601	42·2206	−37·0605
600	5·4448	5·2074	43·2132	−38·0058
800	5·3887	5·2608	44·7731	−39·5123
1000	5·3133	5·2788	45·9674	−40·6886
2000	5·1002	5·2320	49·5700	−44·3380
3000	5·0339	5·1752	51·6232	−46·4480
4000	5·0070	5·1361	53·0672	−47·9311
5000	4·9941	5·1088	54·1832	−49·0744

The values of the heat capacity and free-energy function differ only slightly from those given above. The value of the entropy at 298·16° is close to that given by Kelley, viz. 39·47 ± 0·01 g.-cal./deg.g.-atom.[45]

Detailed tables are also available of values in British units for the heat capacity, enthalpy, enthalpy function and reduced entropy ($s + R \ln P$), of monatomic chlorine in the range 100 − 5000°Rankine.[46]

The following estimates have been made of the 'chemical constant' of atomic chlorine:-

Authors	Date	Chemical Constant	Derived from
Henglein[47]	1922	0·68 0·93 1·5	Thermal dissociation of Cl_2 (3 methods of calculation)
Wohl[8]	1924	1·66 ± 0·30	E.m.f. of heavy-metal cells
Trautz & Ader[44]	1934	1·340	Thermal dissociation of Cl_2

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ELECTRICAL AND MAGNETIC PROPERTIES. PROPERTIES OF CHLORINE IONS

Dielectric Constant.

The dielectric constant of chlorine gas was calculated from a dispersion formula to be 1·00152 at N.T.P. A less certain value, based on the atomic refraction of chlorine in organic compounds, is 1·00160.[1] The dielectric constant of ionized chlorine, tested in the wave-length range 400 – 500 cm., is always slightly less than unity.[2]

Kanda[3] found the following values for the dielectric constant of carefully purified liquid chlorine (see Mellor, II, 65):-

Temp., °K.	208·00	210·51	215·60	220·61	227·90	235·50	239·96
ϵ	2·147	2·139	2·123	2·104	2·088	2·059	2·048

Dipole moment.

The values of the molecular polarization varied irregularly with temperature between 11·94 and 12·00, so that the dipole moment could be taken as zero, in keeping with the symmetry of the molecule.[3] The results of earlier workers,[4-6] who respectively calculated values of 0·79, 0·23 and 0·13 D. for the dipole moment, cannot be accepted.

Molecular Polarizability.

Stuart gave for the mean molecular polarizability of chlorine the value 4·61 × 10^{-24} c.c. (values for the three principal axes were respectively 6·60, 3·62 and 3·62 × 10^{-24} c.c.).[7] The polarizability of the ion is referred to later (see page 348).

Breakdown Voltage.

The sparking voltage in chlorine gas (flowing through a 10-cm. gap between a tubular and a disc electrode) is 58 kV., with 50-cycle a.c.[8] The corona discharge from a wire in the gas at N.T.P. sets in when the potential gradient (50-cycle a.c.) is[9] 85 kV./cm. Negative ions are formed during the electrical breakdown in chlorine.[10]

Ionization Potential.

The ionization potential of the chlorine atom was estimated by Piccardi, from consideration of relations with other elements in the periodic system, to be 12·26 volts.[11] Wicke's more recent value is 12·90 volts, and his values of the potentials required for the production of more highly charged ions are (in volts):[12]

Cl^{II}	23·7	Cl^{III}	39·9	Cl^{IV}	53·5	Cl^{V}	67·8	Cl^{VI}	(97)
Cl^{VII}	114·3	Cl^{VIII}	346·6	Cl^{IX}	398·8	Cl^{X}	~473		

Finkelnburg[13] gives the following potentials, derived from spectroscopic data, for the production of multiply charged positive ions (in volts):-

Cl^{IV}	53·3	Cl^{VI}	96·75	Cl^{X}	455·8	Cl^{XI}	531·4	Cl^{XII}	594·0
Cl^{XIII}	656·6	Cl^{XIV}	749·6	Cl^{XV}	808·2				

Ionic Mobility

The mobilities of the positive and negative ions in pure chlorine gas are[14] respectively 0·654 and 0·510 cm./sec. per V./cm. (An earlier estimate[15] for the negative ion was 0·73 cm./sec.per V./cm.). In mixtures with other gases, chlorine in small amounts has the effect of reducing the mobility of the negative ion below that of the positive ion.[14,16-19] (For the mobility of chlorine ions in solution, see below).

Refs. p. 350

Electric Discharge Phenomena.

Holst and Oosterhuis observed that during a discharge in chlorine between a glow cathode and a cold anode, the chlorine was attracted more by the anode than by the cathode. This was attributed to the formation of negative chlorine ions, the positive ions first formed soon acquiring electrons owing to their high electron-affinity.[20]

Noyes found that the luminous discharge through chlorine, at a pressure about 0·03 mm., disappeared when the applied potential was a multiple of 8·2 V. He suggested that this voltage corresponded to that required for the formation of a molecular ion.[21]

Chlorine which has been subjected to a silent discharge possesses a temporarily increased chemical reactivity. This is discussed in the sub-section on Chemical Properties (see page 382).

The voltage across a carbon arc in chlorine at 700 mm. is only about $\frac{1}{3}$ of that in air, and amounts to 0·7 V. per mm. of arc. Above 4 amp., the voltage changes only 8 – 9% when the current is more than doubled.[22]

When chlorine, through which a discharge current is passing, is irradiated, an instantaneous diminution of the current occurs.[23-25] This effect has been intensively studied by Joshi and other Indian workers, and it has been attributed to a photo-electric action on an adsorbed layer formed under the discharge.[26,27] (The effect is not peculiar to chlorine). When chlorine is subjected to X-rays of 20 – 100 kV. energy, secondary and also tertiary electrons are emitted (as with various other gases).[28,29]

The emission of electrons during certain chemical reactions of chlorine is referred to in the sub-section on Chemical Properties (see page 385).

Electron Affinity.

The electron affinity of the chlorine atom, i.e. the heat evolved in the reaction $Cl + e \longrightarrow Cl^-$, has been derived from data obtained as listed in the following table. (Where necessary, the values in the table have been converted from electron-volts to kg.-cal./g.-atom).

Method	Electron Affinity kg.-cal./g.-atom	Reference
Ionization potential of HCl	111, 98	30, 31
Thermal dissocn. of Cl_2, etc.	73	32
Convergence limit in Cl discharge spectrum	89·3	33
Calcd. entropy of Cl^- in soln.	(17)	34
Consideration of isoelectronic series Ca^{++}, K^+, A, Cl^-	69	35
Absorption spectra of alkali chloride vapours	90 ± 1	36
Lattice energies of alkali chlorides	86·5, 83·0	37, 38
Empirical extrapolation from ionization potentials	85	39
Analysis of AlCl bands	>99 <103	40
Ions in KCl and NaCl vapours	86·6	41
Ionization of Cl atoms on W surface at 2000°K.	92·7 85·84	42, 43
Collisions of NaCl, KCl, RbCl and CsCl mols. with W surface at 2300 – 2600 °K.	85·5 to 87·1 85·3 ± 2·3	44 45
X-Ray absorption by alkali chlorides	85	46

The value preferred in the latest Landolt-Börnstein tables is 3·78 e.V. ≡ 87 kg.-cal./g.-atom.[47] From the U.S. Bureau of Standards tables, values of 85·81 and 87·31 kg.-cal./g.-atom can be deduced for the electron affinity at 0° and 298°K, respectively.[48]

In a theoretical study of the collision of electrons with chlorine atoms, Massey and Smith found that the capture cross-section of the atom falls from a high value at small electron energies to a minimum value of $2{\cdot}0 \times 10^{-22}$ sq.cm. at an energy of 2e.V., rises to a maximum of $3{\cdot}5 \times 10^{-22}$ sq.cm. at 13 e.V., and thereafter diminishes again.[49]

Wahlin found 10^{-3} as the value of the probability of attachment of an electron to a chlorine molecule on collision,[15] whereas Bradbury found that this probability has a maximum value of 0·0026 for $X/p = 7$ (where X is the potential gradient in V./cm., and p is in mm.).[50] On the other hand, the collision of slow electrons with chlorine molecules is reported to be highly elastic, only 0·1% of the energy being lost in a collision at an electron velocity in the range $3 - 5{\cdot}5 \times 10^7$ cm./sec.; the mean free path of an electron moving initially at a speed of 8×10^7 cm./sec. in chlorine is 0·04 cm.[51] The collision cross-section for the scattering of electrons of energy 2 – 50 e.V. by chlorine molecules varies between 8 and $2{\cdot}1 \times 10^{-14}$ sq.cm., with a very marked maximum for an energy of 7·0 e.V.[52]

A quantity related to the electron affinity of an atom is its electronegativity. As derived by Pauling from consideration of the 'extra ionic energy' of bonds between unlike atoms, the value for chlorine is 3·0 on a scale which gives 2·1, 3·5 and 4·0, respectively, for hydrogen, oxygen and fluorine atoms.[53] Mulliken, however, defined electronegativity as the average of the ionization energy (in a particular valence state) and the electron affinity; the value obtained for chlorine (p^5, V_1 state) is then 9·81 ± 0·02 e.V. (2·69 e.V. relative to the hydrogen atom as zero).[54]

Proton affinity of Cl^- ions.

This quantity, which is the energy evolved in the reaction $H^+_{gas} + Cl^-_{gas} \rightarrow HCl_{gas}$, can be calculated from the ionization potential of the hydrogen atom, the electron affinity of the chlorine atom, and the dissociation energies of H_2, Cl_2 and HCl molecules. It has been estimated by various authors to have the values 326, 327, 321 – 328 and 323 kg.-cal./g.-ion, respectively.[55-58]

Hydration of Cl^- Ions.

Estimates of the number of water molecules attached to Cl^- ions in solution, by various methods, give values ranging from 0 to 4.[59]

An early estimate of the heat of hydration of the ion was 161 kg.-cal./g.ion.[34] More modern values are in the range 64·5 – 88 kg.-cal./g.-ion.[59] The Bureau of Standards tables give a value for the heat of formation of Cl^-_{aq}, $\Delta H_{298} = -40{\cdot}023$ kg.-cal./g.-ion, relative to that of H^+_{aq} as zero.[48]

For the entropy of hydration of Cl^-, Kapustinsky found 13·50 g.-cal./deg. g.-ion, at 25°C., referred to $S^0[H^+] = 0$.[60] Gapon calculated in various ways values ranging from 13·7 to 15·4 g.-cal./deg.g.-ion.[61]

Miscenko made the following estimates of the enthalpy and free energy of solvation of Cl^- ions by water and alcohols.

Solvent	$-\Delta H$ kg.-cal./g.-ion	$-\Delta G$ kg.-cal./g.-ion. (Born Equation)	$-\Delta G$ kg.-cal./g.-ion (Bjerrum Equation)
Water	88	87	89
Methyl alcohol	89	86	90
Ethyl alcohol	90	85	91

It has been asserted that dubious assumptions were made in deriving these results.[62]

Polarizability.

The polarizability of the free chlorine ion is given as $\alpha^{D}_{Cl^-} = 3{\cdot}00\ A^3$., or as $\alpha/r^3 = 0{\cdot}51 \times 10^{-24}$ (r is the ionic radius).[63] Earlier values for α were 3·53, 3·66 and 3·05 A^3., respectively.[64-66]

Mobility of Aqueous Ions.

The mobility of aqueous chlorine ions has been determined by conductance studies on solutions of hydrochloric acid or of alkali-metal chlorides.[67-71] The agreement between recent workers is very close; hence it will suffice to quote the following figures as representative:[67]

Temperature, °C.	15	25	35	45
Mobility, l_{∞} $_{Cl^-}$	61·4	76·35	92·2	108·9

The mobility of the ions in aqueous ethyl alcohol at 25° has values as follows:[72]

Mol. % EtOH	2·17	10·83	17·19	46·87	93·55
Mobility, l_{∞} $_{Cl^-}$	60·2	34·2	28·2	23·2	22·4

Electrode Potentials.

The normal reversible potential at 25°C. (between chlorine gas at 1 atm. and a solution containing chlorine ions at unit activity) was found by Randall and Young to be 1·3583 V.,[73] virtually the same as Lewis and Rupert's value (Mellor, II, 65). Schmid found 1·360 V. for the e.m.f. between hydrogen and chlorine diffusion electrodes in N -HCl at 20°C.[74]

On the basis of assumptions concerning equilibria between chlorine, hypochlorous acid, and chloride and hypochlorite ions, Høye[75] found the electrode potential of chlorine in aqueous solution to be expressible by the equation:-

$$E = 1{\cdot}3434 - 0{\cdot}029 \log\left[\frac{4{\cdot}06 \times 10^{-4}}{a_{H^+}}\,\frac{f_{Cl^-}}{f_{HOCl}} + \frac{4{\cdot}22 \times 10^{-10}}{a^2_{H^+}}\right]$$

where a_{H^+} is the H^+-ion activity and f_{Cl^-} and f_{HOCl} are activity coefficients for Cl^- and HOCl respectively. The equation is inaccurate for pH values above 5.

Overvoltage is commonly observed during electrolysis of solutions containing chlorine ions, and the technical importance of this phenomenon is explained in the section on the electrolytic production of chlorine (see page 278). As an example of overvoltage measurements, figures from the work of Knobel et al.[76] are given in Table XIII.

TABLE XIII.- CHLORINE OVERPOTENTIALS AT 25°C.(V.)

Current Density amp./cm.^{2}	Electrode Materials		
	Platinized Platinum	Smooth Platinum	Graphite
1·1	0·0060	0·008	–
40	–	–	0·186
100	0·026	0·0540	0·251
500	0·049	0·161	0·417
1131	–	–	0·535
1350	0·090	0·263	–

Other studies of chlorine overvoltage were made by Newbery,[77] Stender et al.,[78] and Chang and Wick.[79] Polarization voltage at a chlorine electrode can be reduced by the action of ultrasonic waves.[80-82]

According to Hartley et al., the electrode potential at 25°C. of chlorine in methanol is 1·128 V., and in ethanol 1·060 V., with respect to hydrogen as zero in the same solvent.[83]

Table XIV gives values for the activity coefficients of aqueous chlorine ions:[84]

TABLE XIV. - ACTIVITY COEFFICIENTS OF CHLORIDE ION IN WATER

Total ionic concentration	Activity coefficient	Total ionic concentration	Activity coefficient
0.001	0.975	0.02	0.899
0.002	0.964	0.05	0.85
0.05	0.945	0.1	0.805
0.01	0.925	0.2	0.755

Occurrence of Positive and Multiply Charged Chlorine Ions in the Liquid Phase.

In contrast with its normal appearance as an anion in an electrolyte, chlorine appears as a cation in the electrolysis, in pyridine solution, of N-chlorinated imides such as N-chlorosuccinimide.[85] This phenomenon probably depends on co-ordination of the Cl^+ ion with pyridine (a compound with the structure $[Cl,(C_5H_5N)_2]^+(NO_3)^-$ can be isolated in solid form, m.p. 77·8°, after reaction of chlorine with silver nitrate in a mixture of dry pyridine and dry chloroform).[86] No positive chlorine ions can be detected in aqueous hypochlorous acid, by a method which gives a positive result with hypobromous acid.[87] The subject of positive halogen ions has been discussed by Sidgwick, who calculates that, owing to the ionic dissociation of water and the occurence of the dissociation $HOCl \rightleftharpoons H^+ + ClO^-$, the maximum value which the constant of the dissociation $HOCl \rightleftharpoons Cl^+ + OH^-$ could have in a normal hypochlorous acid solution is 3×10^{-21}, corresponding to $[Cl]^+ = 5{\cdot}5 \times 10^{-11}$. In 0·01 N-HOCl, the corresponding maximum figures would be 3×10^{-17} and $5{\cdot}5 \times 10^{-10}$ respectively.[88]

It has been suggested that polymeric negative chlorine ions, Cl_2^{2-} and Cl_4^{4-}, are present in fused silver and lead chlorides respectively.[89]

The trichloride ion, Cl_3^-, is discussed in the section on chlorine solutions (see page 367).

Magnetic Properties of Chlorine and its Ions.

From measurements of the Faraday effect on aliphatic halogen derivatives, de Mallemann and Gabiano found for the atomic magnetic rotatory power of chlorine the value 33×10^{-2} (unit unspecified), as compared with 108×10^{-2} for the Cl^- ion.[90] In a later paper they quoted the former result as $9{\cdot}0 - 9{\cdot}5 \times 10^{-5}$ radians, and compared it with $10{\cdot}4 \times 10^{-5}$ radians obtained by measurements of magnetic rotatory power made on chlorine itself at 998 and 250 mm.[91] Elsewhere Gabiano gave 0·71 as the value of the molecular magnetic rotation of chlorine gas, measured in (min. of arc). cm.^{2}/gauss-mole.[92] Okazaki measured the Faraday effect for salt solutions and determined the values of a function $\Phi = Mnw\lambda^2/s(n^2 + 2)^2$, where n and w are respectively the refractive index and Verdet's constant for light of wave-length λ, M is the mol.wt. and s the density. The contribution to the value of Φ due to a chlorine ion was calculated to be $11{\cdot}17 \times 10^{-14}$ (cf. $-1{\cdot}41 \times 10^{-14}$ for a H^+ ion, $0{\cdot}61 \times 10^{-14}$ for a K^+ ion).[93]

Values given for the atomic diamagnetic susceptibility of (combined) chlorine, derived chiefly from measurements on organic compounds, are respectively $20{\cdot}1 \times 10^{-6}$ and $18{\cdot}4 \times 10^{-6}$.[94,95] The values selected by Klemm for the diamagnetic susceptibility of the Cl^- ion, in a review of the available data, were 28×10^{-6} for the free ion, $28{\cdot}0 \times 10^{-6}$ for the ion in aqueous solution, $26{\cdot}0 \times 10^{-6}$ for the ion in crystals with co-ordination-number 6, and $25{\cdot}7 \times 10^{-6}$ in crystals with co-ordination-number 8.[96] In a later review, Pacault listed 30 values for the diamagnetic susceptibility of this ion, ranging from 20·1 to

24·2 in crystals, 17·6 to 25·1 in solution, 21·8 to 28 in the free state (experimental) and 23·6 to 41·3 in the free state (calculated theoretically): all these values are to be multiplied by 10^{-6}.[97]

According to Bhuyan, a small increase in diamagnetic susceptibility occurs when chlorine is exposed to light, especially of the violet end of the spectrum. This is contrary to expectation, since irradiation gives rise to paramagnetic atoms of chlorine.[98]

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ATOMIC WEIGHT AND ISOTOPES OF CHLORINE, DIMENSIONS OF THE ATOM, ETC.

Atomic Weight.

The following determinations of the atomic weight were made in the period surveyed in this Supplement (the values are expressed on the usual chemical scale).

Authors	Year	Basis	Result
Magnus & Schmid[1]	1922	Difference between limiting density of chloroform vapour & $\frac{1}{6}$ that of benzene vapour.	35·455
Moles & Clavera[2]	1922	Ratio $NaNO_3$:NaCl (evapn. of $NaNO_3$ with HCl)	35·457
Lorenz & Bergheimer[3]	1924	Ratio Ag:AgCl (synthesis of AgCl)	35·453
Zintl & Meuwson[4]	1924	Ratio $NaNO_3$:NaCl	35·457 ±0·0006
Batuecas[5]	1925	Density of CH_3Cl (ex PCl + MeOH or $Me_4N.Cl$)	35·470
Moles[6]	1925	(Review)	(35·458)
Moles[7]	1926	(Review)	(35·458)
Batuecas[8]	1926	Density of CH_3Cl (ex $Me_4N.Cl$)	35·465
Zintl & Goubeau[9a]	1927	Ratio KNO_3:KCl, combined with KCl:Ag and AgCl:Ag ratios	35·456 ±0·0003
Hönigschmid et al.[9b]	1927	(a)Direct synthesis of AgCl (b)$CCl_4 \rightarrow HCl \rightarrow AgCl$	35·457 35·457
Hönigschmid et al.[9c]	1931	Correction of preceding data.	35·456
Scott & Johnson[10]	1929	Ratio NOCl:Ag	35·4565
Moles[11]	1929	(Review)	(35·457)
Honigschmid & Schlee[12]	1936	Ratio $AgNO_3$:AgCl	35·457

In addition to the above, Blears and Metrrick (1947) using a mass-spectrograph obtained values of 35·452 and 35·462 by different methods of scanning. These results were regarded by the authors as a check on their instrument rather than as an atomic weight determination.[13]

The internationally accepted value of the atomic weight has remained unchanged at 35·457 for many years.[14,15] This value is identical with that thought by Brunauer (1913) to be the most probable (Mellor, II, 104), a tribute to the skill and care of the earlier workers at Harvard and elsewhere.

Isotopes.

The earliest work of Aston with the mass spectrograph revealed the existence in normal chlorine of the isotopes of masses 35 and 37 (Mellor, II, 105). With one exception, where it was suggested that the isotopic masses are 34 and 36,[16] all subsequent work has confirmed Aston's findings. The existence of the two chlorine isotopes has been demonstrated also by observation of doublets in the band spectrum of hydrogen chloride[17,18] and of silver chloride vapour [19] and further by magneto-optical observation of chlorine in aqueous solution[20] and by mass analysis of negative chlorine ions emitted from oxide-coated cathodes.[21,22]

In his first work, Aston obtained an indication of a third isotope, of mass 39, but later concluded that this isotope was not present.[23] Subsequent workers, however, claim to have detected ^{39}Cl by observation of the infra-red spectrum of hydrogen chloride, by the mass-spectrograph, and by the magneto-optical method.[20,24-27] Other workers again could not detect this isotope and concluded that if it exists in normal chlorine it must be present only in very small proportions; one investigator estimates that the amount present cannot exceed 1 part in 20,000.[18,19,28] It is now believed that there is no certain evidence for the existence of any stable chlorine isotope other than ^{35}Cl and ^{37}Cl.

Refinements in mass-spectrographic technique have enabled the exact atomic masses of ^{35}Cl and ^{37}Cl (on the scale ^{16}O = 16·0000), and their abundance ratio, to be determined. Table XV gives these data and also the atomic masses found by other physical methods.

TABLE XV.- ATOMIC MASSES OF ISOTOPES OF CHLORINE DETERMINED BY PHYSICAL METHODS

Authors	Year	Atomic Masses ^{16}O = 16		Abundance Ratio ^{35}Cl / ^{37}Cl
		^{35}Cl	^{37}Cl	
Aston[29]	1931	34·982	36·980	3·0 – 3·1
Kallmann & Lasareff[27]	1933	–	–	3·24
Bainbridge[30]	1933	34·9796 ±0·0012	36·9777 ±0·0019	–
Aston[31]	1936	34·9800 ±0·0008	36·9775 ±0·0008	–
Nier & Hanson[28]	1937	–	–	3·07±0·03
Menzies[32]	1938	–	–	3·15*
Okuda *et al.*[33]	1940	34·97903±0·00038	36·97786±0·00036	–
Pollard[34]	1940	34·98107 †	36·97829 †	–
Okuda[35]	1942	34·97881±0·00020	36·97766±0·00012	–
Gibert et al.[36]	1944	34·98054 ‡	–	–
Madorsky & Straus[37]	1947	–	–	3·12
Blears & Mettrick[13]	1947	–	–	✠{ 3·15±0·04 3·07±0.02

* Estimated from the Raman spectrum of carbon tetrachloride.

† Derived from the energies of β-rays emitted in transmutations of these isotopes.

‡ Derived from energy relations in the reaction between neutrons and ^{35}Cl nuclei.

✠ Alternative values, according to the method of operating the mass spectrograph.

For the 'packing fractions' of the chlorine isotopes, i.e. the value of the quantity (atomic mass − mass number) × 10^4/(mass number), Aston[31] gave the values −5·71 and −6·10 respectively for ^{35}Cl and ^{37}Cl: Okuda's[35] corresponding values were −6·06 and −6·03.

The ^{35}Cl/^{37}Cl abundance ratio[28] required by the accepted value of the atomic weight (35·457) is 3·10 (or 3·18 according to Aston's earlier measurements of the masses).[29] For technical reasons associated with intensity measurements in the mass spectrograph, and because of a slight uncertainty in the relation between the 'physical' (^{16}O = 16) and 'chemical' (O = 16) scales of atomic weight, the mass-spectrographic method has not in the case of chlorine been considered precise enough for an exact check of the atomic weight as determined by the very accurate chemical methods.[29,38]

With the object of testing whether the ^{35}Cl/^{37}Cl abundance ratio in naturally occurring chlorine is always the same, numerous careful determinations of the atomic weight of chlorine, derived from the most diverse sources, were made in the years following the discovery of the isotopes. These sources included Norwegian chlorapatite, Canadian sodalite, and sodium chloride from a Central African desert,[39] apatite of great geological age,[40] Balrue apatite,[41] ammonium chloride from Vesuvius,[42] a meteorite and three minerals of non-marine origin,[43,44] 'shale balls' associated with an Arizona meteorite,[45] urine[46] and salt from four different strata of the Alsace deposits.[47] In all cases the atomic weight was found to be the same as the internationally accepted value, within the error of the determinations. It is to be concluded that the isotopes have remained intimately mixed in their present proportions, at least for the greater part of the earth's history.

Urey has pointed out, however, that owing to the possible effect of isotope exchange reactions, the constancy of the atomic weight of chlorine in nature should not be considered absolute, because calculations of equilibria for exchange reactions involving the chlorine isotopes (see page 358) show that it is theoretically possible for the abundance ratio in the reactants to be shifted sufficiently to cause changes of atomic weight as great as 0·031 unit. The observed apparent constancy may be due largely to careful duplication of purification procedures.[48,49] The effect of isotopes on the entropy and free-energy function of chlorine has been referred to in the sub-section on thermodynamic properties (see pages 339,341).

Radioactive Isotopes of Chlorine.

In addition to the two stable isotopes, there are the radioactive isotopes, shown in Table XVI, which have been made artifically by nuclear reactions.

TABLE XVI. - RADIOACTIVE ISOTOPES OF CHLORINE

Isotope	Process of formation	Properties		
		Half-life	Particles emitted (energies in MeV)	References
^{33}Cl	^{32}S(d, n) ^{33}S(p, n)	2·8 sec, 2·4 ± 0·2 sec.	β^+(4·13)	50, 51
^{34}Cl	^{35}Cl(n, 2n) ^{31}P(α, n) etc.	33 min., 38 min.. 33·2 ± 0·5 min.	β^+(1·3, 2·58, 4·55), and γ	52–55
^{36}Cl	^{35}Cl(n,γ) ^{35}Cl(d, p)	> 10^3 yr., 0.44 ± 0·05 × 10^6 yr.	β^-(0·64), ? and *K*	56, 57
^{38}Cl	^{37}Cl(n,γ) etc.	37 min., 38 min., 37·29 ± 0·04 min.	β^-(1·11, 2·77, 4·81), and γ	55, 58–60
^{39}Cl	^{40}A(γ, p)	55·5 ± 0·2 min.	β^-(1·65, 2·96), and γ	61, 62

In the second column of the table the process of formation of each isotope is indicated in the conventional manner, i.e. the first symbol is the nucleon bombarded, the second is the bombarding particle or ray, and the third is the particle or ray emitted along with the chlorine isotope formed (β^+ = positron, β^- = electron, γ = γ-ray photon, p = proton, d = deuteron, n = neutron; *K* referring to the absorption of a *K*-electron into the nucleus).

A report of the existence of a ^{36}Cl isotope of half-life 50 min. (a β^-emitter)[63] lacks any confirmation by other workers.

For further information on these isotopes, the reader is referred to the radiochemical section (see page 963), and to published tables of isotopes.[64,65]

Separation of the Chlorine Isotopes.

Among the earlier attempts to separate the stable chlorine isotopes, the most notable work was that done between 1920 and 1928 by Harkins and his collaborators, employing fractional diffusion of hydrogen chloride through porous porcelain pipe-stems. The procedure was to pass pure hydrogen chloride through 12 metres of pipe at such a rate that 95% of the gas diffused through the walls. The remaining 5%, which traversed the tube length, was treated similarly, and so on for four cycles in all, giving a final 'heavy' fraction containing chlorine of atomic weight 35·512, i.e. 0·055 unit higher than normal. Conversely a 'light' fraction could be obtained, containing chlorine of atomic weight 35·418, or 0·039 unit lower than normal. The efficiency of isotope separation was about 60% of that predicted by Rayleigh's theory of diffusion.[66-72]

Brönsted and Hevesy, by repeated fractional distillation of 8·6 M-hydrochloric acid in high vacuum at −50°C., obtained heavy and light fractions which, after conversion into sodium chloride, exhibited density differences indicating 0·024 unit difference in atomic weight (6·5% change in the isotopic ratio).[73] This result was confirmed by Harkins.[67] Other workers attempted without success to obtain isotopic separation by fractional distillation of liquid chlorine or of chloromethanes,[74,75] but Stedman, by slow distillation of carbon tetrachloride through a column rated at 110 'theoretical plates', at a 3000 : 1 reflux ratio, obtained light and heavy fractions in which the atomic weights of chlorine differed by 0·048 unit; a similar treatment of methylene chloride gave a lesser separation.[76]

Kuhn and Martin tried a photochemical method of separation which depended on prolonged irradiation of phosgene by light of wave-length 2816·18 A. (from an aluminium arc), this wave-length being close to one of the absorption bands of $CO^{35}Cl_2$, but somewhat separated from the corresponding bands of $CO^{35}Cl\,^{37}Cl$ or $CO^{37}Cl_2$. The liberated chlorine had an atomic weight 0·025 unit lower than normal.[77] Similarly, irradiation of chlorine dioxide by light of wave-length 3663·27 A. (from a mercury lamp), corresponding to one of the absorption bands of $^{35}ClO_2$, yielded chlorine of atomic weight 0·016 unit lower than normal provided that the vessel was packed with Raschig rings to minimize the propagation of reaction chains.[78]

By oxidizing hydrochloric acid with a mixture of nitric and sulphuric acids containing potassium permanganate until 10·5% of the original hydrochloric acid remained, Ogawa obtained a residual acid containing chlorine with an atomic weight 0·014 unit lower than normal. Similarly, by oxidation with potassium permanganate and sulphuric acid until only 5·1% of the original hydrochloric acid remained, he obtained a reduction in atomic weight of 0·037 unit. This confirmed Ogawa's theory that the heavier isotope should concentrate in the more positively polarized state i.e. free chlorine.[79]

By interaction of pure carbon tetrachloride with sodium amalgam until the former was half decomposed, and repeated distillation of the residue to remove a trace of by-product (presumably hexachloroethane), Bradley[80] obtained carbon tetrachloride with a slightly increased density, corresponding to an increase in the proportion of ^{37}Cl by a factor of 1·0013.

Evidence of isotope separation by ionic-migration was observed when chlorine ions were caused to migrate a distance of 10 – 20 metres into a gel containing sodium hydroxide.[81] More recently, by means of an electromigration cell in which chlorine ions were transported from a sodium chloride solution into a sodium hydroxide solution lying beneath, with counter-current flow of the liquid to maintain a static NaOH/NaCl boundary, Madorsky and Straus[37] obtained after a run of 474 hours a chloride sample in which the proportion of ^{35}Cl had been increased from 75·76% to 80·7%.

Yacoubyan electrolyzed a solution, containing initially 3N-hydrochloric acid and 20% sodium chloride, until the amount of Cl^- ion had diminished from 36 kg. to 24 g. The atomic weight of the chlorine in the residue increased by 0·016 unit.[82] On the other hand no evidence of isotope separation was found on examining the residues from a bath which had been used continuously for

30 years for the electrolytic production of potassium chlorate, or in sodium chloride and alkaline earth chloride residues from the electrolytic production of sodium. A sample from a chlorine still which had been used over a long period indicated that the residues had possibly been enriched in ^{37}Cl to the extent of 0·1%.[83]

Johnston and Hutchinson determined the electrolytic separation coefficient α (defined as $d\log(^{35}Cl)/d\log(^{37}Cl)$) for the electrolysis of aqueous sodium chloride with a platinum anode. The value obtained was 1·0060 ± 0·0005, as compared with the value 1·0068 calculated from Yacoubyan's work.[84] A later determination of α gave the value 1·0063, constant over the range 15 – 40°C. and independent of current density; in this case the change of atomic weight after 85% of the salt had been consumed was 0·0046 unit.[85]

Urey and his collaborators found that a slight enrichment of ^{35}Cl in the liquid phase can occur by an isotope-exchange reaction between hydrogen chloride and its aqueous solution.[86] Urey has also estimated the possibility of isotope-ratio changes in several other exchange reactions involving chlorine isotopes (see page 354).

By centrifuging liquid ethyl chloride at high speed at 700°K., and gradually withdrawing vapour by evacuation through the centrifuge shaft, Armistead and Bearns obtained first and last fractions which differed in isotope ratio by 12%. This result agreed with theoretical predictions.[87]

Virtually complete separation of the chlorine isotopes was first achieved by Clusius and Dickel (1938), using the thermal gas-diffusion principle.[88] This method depends on the fact that, with a mixture of gases contained in a vertical cylinder provided with a heating element along its axis and having its wall externally cooled, a greater concentration of the lighter molecules of the mixture tends to be produced at the axis of the cylinder and conversely a greater concentration of the heavier molecules at the wall. Hence, owing to convection up the axis and down the cooled outer wall, the lighter and heavier molecules tend to be concentrated at the top and bottom of the cylinder respectively, so that separated fractions can be gradually drawn off. (A full explanation of the mechanism of the effect requires consideration of the more complex aspects of the kinetic theory of gases).[89]

Clusius and Dickel operated with hydrogen chloride since the separation factor, which depends on the nature of the intermolecular repulsion forces, is more favourable with this gas than with chlorine. They used a series of tubes of 8·4 or 12·8 mm. diameter, having a total height of 36 metres. The temperature gradient was created by means of a platinum wire of 0·4 mm. diameter, heated at 690 – 740°C., located along the axes of the tubes by means of thin perforated platinum plates mounted at 60 cm. intervals. The process was operated continuously, several days being required to obtain the first yield of nearly pure ^{35}Cl, but several weeks for the first yield of ^{37}Cl. Their papers give details of the many factors affecting the degree of separation and the rates of transport of the isotopes towards the ends of the tubes. The daily output achieved was 16 c.c. of gaseous hydrogen chloride in which the chlorine had an atomic weight of 34·979 (99·6% of ^{35}Cl), together with 8 c.c. of gas in which the chlorine had an atomic weight of 36·956 (99·4% of ^{37}Cl). The energy required per mole of hydrogen chloride separated was $3{\cdot}7 \times 10^{10}$ g.-cal., or 1.1×10^{8} times the theoretical work done in separating the molecules (12 times the amount calculated for the actual process).[90-93]

The thermal-diffusion method has also been applied to hydrogen chloride by later workers who, however, did not carry it to the point of achieving so good a separation of the isotopes.[94,95] It has also been used with carbon tetrachloride vapour, but the process was not carried beyond the point where there was 0·5% change in the isotope ratio.[96]

Another method which has been used to separate the chlorine isotopes completely, though in small amounts, is electromagnetic separation in a calutron (a type of cyclotron). Cuprous chloride was the raw material used, and the beams of mass number 98 ($^{63}\mathrm{Cu}^{35}\mathrm{Cl}^{+}$) and 102 ($^{65}\mathrm{Cu}^{37}\mathrm{Cl}^{+}$) were collected.[47]

Other methods of attempting to separate the chlorine isotopes include fractional absorption of hydrogen chloride in water or aqueous ammonia,[98] fractional desorption of hydrogen chloride from charcoal,[99] fractional dialysis of sodium chloride through membranes,[100] solution of hydrogen chloride in ferric chloride solutions, or the formation of ‘solid salts of magnesium oxychloride and carnallite’,[101] and causing sodium chloride crystals to flow in counter-current against a saturated solution of the salt in aqueous methanol.[102] In all these cases the degree of separation achieved was zero within the experimental error, but probably in some instances a positive result could have been obtained with more refined technique. especially in the atomic-weight determinations.

Exchange Reactions with Chlorine Isotopes.

As with many of the other elements, exchange reactions involving natural and radioactive chlorine isotopes have been used as a tool for investigating reaction mechanisms, physical and chemical equilibria, etc. Examples of

TABLE XVII. - EQUILIBRIUM CONSTANTS FOR EXCHANGE REACTIONS BETWEEN PAIRS OF IONS OR MOLECULES CONTAINING CHLORINE ISOTOPES

	$\frac{^{37}\mathrm{ClO}_4^-}{^{35}\mathrm{ClO}_4^-}$	$\frac{^{37}\mathrm{ClO}_3^-}{^{35}\mathrm{ClO}_3^-}$	$\frac{^{37}\mathrm{ClO}_2}{^{35}\mathrm{ClO}_2}$	$\left(\frac{^{37}\mathrm{Cl}_2}{^{35}\mathrm{Cl}_2}\right)^{1/2}$	$\frac{\mathrm{H}^{37}\mathrm{Cl}}{\mathrm{H}^{35}\mathrm{Cl}}$	Temp. °K.
Values of Q_2/Q_1	1·0972	1·0551	1·0360	1·0086	1·0050	273·1
	1·0847	1·0478	1·0313	1·0074	1·0046	298·1
	1·0521	1·0291	1·0185	1·0043	1·0032	400
	1·0353	1·0196	1·0130	1·0028	1·0024	500
	1·0253	1·0140	1·0094	1·0019	1·0019	600
	Values of *K*.					
$\frac{^{37}\mathrm{ClO}_4^-}{^{35}\mathrm{ClO}_4^-}$	(1·000)	1·040	1·059	1·088	1·092	273·1
		1·035	1·052	1·077	1·080	298·1
		1·022	1·033	1·048	1·049	400
		1·015	1·022	1·032	1·033	500
		1·011	1·016	1·023	1·023	600
$\frac{^{37}\mathrm{ClO}_3^-}{^{35}\mathrm{ClO}_3^-}$		(1·000)	1·018	1·046	1·050	273·1
			1·016	1·040	1·043	298·1
			1·010	1·025	1·026	400
			1·007	1·017	1·017	500
			1·005	1·012	1·012	600
$\frac{^{37}\mathrm{ClO}_2^-}{^{35}\mathrm{ClO}_2^-}$			(1·000)	1·027	1·031	273·1
				1·024	1·027	298·1
				1·014	1·015	400
				1·010	1·010	500
				1·007	1·007	600
$\left(\frac{^{37}\mathrm{Cl}_2}{^{35}\mathrm{Cl}_2}\right)^{1/2}$				(1·000)	1·004	273·1
					1·003	298·1
					1·001	400
					$1·000_4$	500
					$1·000_0$	600

such uses are the estimation of the velocities of the forward and reverse reactions in the equilibrium $Cl_2 + Cl^- \rightleftharpoons Cl_3^-$ (see page 384), the demonstration that all five chlorine atoms in PCl_5 are probably equally reactive,[103] and the investigation of the mechanism of reactions involving reduction or oxidation of chlorite ions.[104,105]

Equilibria for some of the simpler exchange reactions of chlorine isotopes were calculated by Urey. If A_1 and B_1 are two molecules containing ^{35}Cl, and A_2 and B_2 are two similar molecules containing ^{37}Cl, then the equilibrium constant for the reaction $aA_1 + bB_2 \rightleftharpoons aA_2 + bB_1$ is expressible by $K = (Q_{2A}/Q_{1A})^a/(Q_{2B}/Q_{1B})^b$, where Q_{2A}, etc., refer to the partition-functions for reactions between A_2 and ^{35}Cl, etc. The Q_2/Q_1 ratios can be calculated with the aid of the symmetry numbers and vibration frequencies of the molecules. Table XVII gives values of Q_2/Q_1 for five ions or molecules, as calculated by Urey for five temperatures, together with the derived values of K for exchange reactions between pairs of these ions or molecules. Where K exceeds unity, the ^{37}Cl isotope will concentrate in the compound listed on the left of the table, and K will tend to infinity as the temperature falls to 0°K. As noted earlier (see page 354), these exchange reactions could lead to appreciable variation in the observed atomic weight of chlorine.[49]

For the interchange of chlorine molecules with each other, i.e. in the reaction $^{35}Cl_2 + {}^{37}Cl_2 = 2{}^{35}Cl^{37}Cl$, the value of ΔE_0° derived from spectroscopic data is 0·18 cm.$^{-1}$ or 0·51 g.-cal./mole, and $\Delta(G^\circ - E_0^\circ)/T$ at 298·1°K. = −2·7549 g.-cal./deg./mole. Hence from the equation $\Delta G^\circ/T = -R \ln K$ the equilibrium constant $K = (^{35}Cl^{37}Cl)^2/(^{35}Cl_2)(^{37}Cl_2)$ has been calculated to have the value 3·9997 at 298·1°K., (the value would be exactly 4 if the formation of each type of Cl_2 molecule were a matter of pure chance). At absolute zero, $K = 0$ and at equilibrium all the molecules would either be $^{35}Cl_2$ or $^{37}Cl_2$.[106]

Further references to exchange reactions of chlorine isotopes will be found in the section on the radiochemistry of chlorine (see page 1013).

Dimensions of Chlorine Atoms, Ions and Molecules.

The covalent radius of the chlorine atom, i.e. the average contribution made by it to the length of a single covalent bond joining it to another atom, is 0·99 A. This value is based on analysis of the spectrum of the chlorine molecule (see page 627), and on the internuclear distance in the chlorine molecule as found by electron-diffraction measurements. The value calculated for a doubly-bound chlorine atom is 0·90 A.[107,108] A more recent estimate is 0·995 A. for the singly-bound atom and 0·89 A. for the doubly-bound atom, these estimates being based on consideration of the packing radii of organic molecules.[109]

Estimates of the radius of the space occupied by a chlorine atom are: from the viscosity of carbon tetrachloride vapour 1·2 A.,[110] from the b.p. of liquid chlorine $\nless$3·2 A.(?),[111] from the parachor 1·44 A.,[112] and from consideration of co-ordination numbers 1·45 A.[113] Pauling gave 1·80 A. as the 'van der Waals' radius of the atom.[107]

The radius of the Cl^- ion, as in alkali-metal chloride crystals, is 1·81 A. this value being derived from X-ray measurements of lattice spacings supplemented by consideration of molecular refractivities or of atomic 'screening constants'.[107] In aqueous solution, this ion has an effective radius about 3 A. (Mellor, II, 65). Estimates of 0·26 A. and 0·49 A. have been made for the radii of the Cl^{7+} and Cl^+ ion respectively.[107] Earlier estimates of 0·96 – 1·17 A. for the radius of the Cl^- ion in crystals[114–116] were based on erroneous estimates of the relative contributions of the positive and negative ions to the lattice spacing.

In the chlorine molecule the inter-nuclear distance is twice the above covalent radius, i.e. 1·98 or 1·99 A. (one measurement by electron diffraction, however, gave 1·995 or 2·009A.).[117] Values calculated for the 'collision' diameter of the molecule from viscosity measurements on the gas (see page 328) are:-

Temperature in °K.	288·8	373	498·7	747·5	v.high
Diameter in A.	5·47	5·13	4·83	4·46	3·68

The value of σ_k derived from critical data and the van der Waals constant b is 3·54 A.[118] A theoretical consideration of the internal pressure and surface tension of liquid chlorine gave 3·69A. as the normal diameter of the molecule, and 3·48A. as the diameter of the sphere impenetrable by another molecule without the application of a very large force.[119]

Calculations of the extent to which the average internuclear distance in the chlorine molecule is increased by the acquisition of vibrational and rotational energy at various temperatures have been made.[120]

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SOLUTIONS OF CHLORINE IN WATER AND OTHER SOLVENTS

Solubility of Chlorine in Water.

Values reported for the solubility of chlorine in water at 25°C. and a partial pressure of 1 atm. are respectively 0·0923 molal[1] (moles per 1000 g. of water) and 0·0921 molar.[2]

Whitney and Vivian[3] determined the solubility over a range of temperatures and pressures by a flow method; their results (here abbreviated) are given in Table XVIII.

TABLE XVIII. - SOLUBILITY OF CHLORINE IN WATER

10°C.		15°C.		20°C.		25°C.	
Partial pressure atm.	Solubility g./l.	Partial pressure atm.	Solubility g./l.	Partial pressure atm.	Solubility g./l.	Partial pressure atm.	Solubility g./l.
0·0601	1·24	0·0581	1·11	0·0665	1·12	0·0621	1·04
0·0660	1·31	0·0611	1·15	0·1195	1·60	0·0655	1·06
0·155	2·28	0·145	2·01	0·260	2·62	0·104	1·39
0·292	3·68	0·291	3·30		2·65	0·109	1·43
0·498	5·41	0·490	4·80	0·490	4·22	0·174	1·89
	5·55	0·951	8·25	0·965	7·25	0·270	2·46
						0·551	3·91
						0·589	4·18
						0·961	6·26

At a chlorine pressure about 1 atm., these results show deviations of 0·3 – 1·1% from those of Winkler.[4] Fig. 2 gives the results graphically and Fig. 3 shows the extent of variation from the results of Adams and Edmonds (below). The total molal concentration (c) of chlorine dissolved is given by the equation $c = Hp + (KHp)^{1/3}$, where H is the partition coefficient of unhydrolysed chlorine between air and water, p is the partial pressure, and K is the hydrolysis constant, (moles/1000 g. water)^2; Whitney and Vivian's values for H at 10, 15, 20 and 25°C. were respectively (in moles/1000 g. water/atm.) 11·6, 9·35, 7·75 and $6{\cdot}23 \times 10^{-2}$ (their values for K are given later, see page 365). A nomograph is available, based on their solubility data.[5]

Among earlier workers, Titov gave the formula $(y - 1{\cdot}748)^3\, x^2 = (72{\cdot}52)^3$ to express the partition of chlorine between water and air at 20°C.; here x is the volume of chlorine per 1000 volumes of air and y is the volume dissolved in the water under the corresponding partial pressure.[6] Adams and Edmonds derived a formula (based on earlier work)[7,8]

$$c = \frac{70{\cdot}9\,\gamma P}{\mu RT} + \left(\frac{K\gamma\, 70{\cdot}9 P}{\mu RT}\right)^{1/3}$$

where c is in moles/l., K is the hydrolysis constant, P is the partial pressure, γ corresponds to H above and μ is a factor correcting for deviation from perfect-gas behaviour. Table XIX gives a selection of the solubility values, calculated with the aid of this formula and Jakowkin's experimental data (cf. Fig. 3). Up to 80°, these values show deviations of –4·2 to + 2·1% from those given in 'International Critical Tables'[14] (the deviation at 90° is 21%).[9]

Various authors have determined coefficients for the rate of continuous solution of chlorine in water, in packed towers. As expected from the low solubility, the rate of solution depends on the temperature and the liquor flow-rate, but not on the gas flow-rate,[9-12] showing that the factor limiting the solution rate is the diffusion of chlorine from a saturated layer of solution in contact with the gas.

The rate of evaporation of chlorine from aqueous solutions stronger than

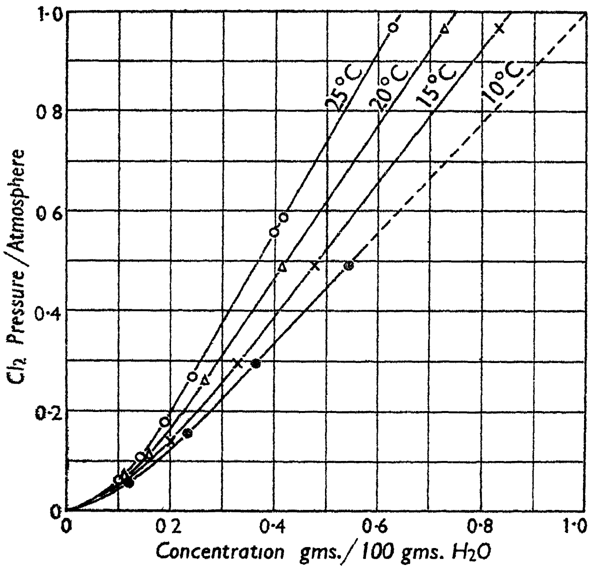

Fig. 2. SOLUBILITY OF CHLORINE IN WATER AT CONSTANT TEMPERATURE

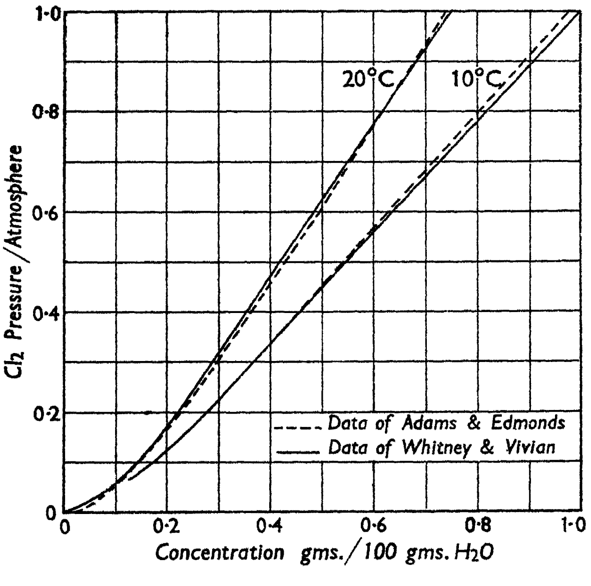

Fig. 3. COMPARISON OF CALCULATED DATA OF ADAMS AND EDMONDS WITH EXPERIMENTAL DATA OF WHITNEY AND VIVIAN

0·001 M. is reported to be controlled by the rate of diffusion of the chlorine to the air/liquid surface. With weaker solutions, the rate depends on the partial chlorine pressure, but not if hydrochloric acid is present.[13]

The solubility of chlorine in aqueous solutions of salts and acids is discussed later (see page 367).

TABLE XIX. - SOLUBILITY (g.Cl per l. of solution) OF CHLORINE IN WATER DERIVED BY USE OF ADAMS AND EDMONDS' FORMULA

Pressure mm.	Temperature, °C.							
	0	10	20	30	40	60	80	100
5	0·488	0·451	0·438	0·424	0·412	0·383	0·351	0·326
10	0·679	0·603	0·575	0·553	0·532	0·492	0·447	0·415
50	1·717	1·354	1·210	1·106	1·025	0·912	0·815	0·747
100	2·79	2·08	1·773	1·573	1·424	1·228	1·085	0·987
250	5·71	3·95	3·19	2·69	2·34	1·914	1·642	1·480
500	*	6·85	5·29	4·30	3·61	2·80	2·35	2·08
750		9·65	7·29	5·80	4·77	3·59	2·96	2·60
1000		*	9·27	7·27	5·89	4·36	3·53	3·07
2000			17·07	13·02	10·22	7·14	5·63	4·78
3000			*	18·73	14·47	9·83	7·54	6·38
4000				24·7	18·84	12·54	9·52	7·94
5000				30·8	23·3	15·26	11·42	9·48

* Chlorine hydrate separates

Chlorine Hydrate.

Bouzat and Azinieres prepared chlorine hydrate by shaking water and pure liquid chlorine together in a sealed tube at 0°, with exclusion of bright light, and allowing the excess of chlorine to evaporate through a capillary opening after being kept overnight. Analysis of the crystals by two methods gave $Cl_2,6H_2O$ as the probable formula.[14] Anwar-Ullah repeated this work and obtained a mean result of $Cl_2,6{\cdot}12H_2O$ from four preparations which were kept 4—9 months before the tubes were opened (the results were more reproducible when long periods were allowed for reaction). He prepared the hydrate also by passing chlorine into water at 0° and sucking the crystals dry in an atmosphere of chlorine in a specially designed filter; again the results of analysis approximated to the formula $Cl_2,6H_2O$, and he attributed the higher degrees of hydration, reported by some of the earlier workers (Mellor, II, 72) to imperfect drying of the crystals or incomplete reaction between water and chlorine.[15]

By application of the Clapeyron-Clausius equation to Roozeboom's values for the vapour pressure of chlorine hydrate above and below 0° (Mellor, II, 72), Harris calculated ΔH = 17870 g.-cal./mole for the dissociation into chlorine gas and water, and 6413 g.-cal./mole for the dissociation into chlorine gas and ice. The difference between these, divided by the molecular heat of fusion of ice, gave 7·97, i.e. approximately 8, as the number of water molecules per molecule of chlorine.[16] Von Stackelberg, however, also using Roozeboom's data, arrived at 15500 and 7100 g.-cal./mole, respectively, for the above heats of dissociation; from these he calculated[17] the number of water molecules per molecule of chlorine to be 5·97, i.e. approximately 6. Bouzat, using unspecified vapour-pressure data, likewise deduced the formula $Cl_2,6H_2O$.[18] It is clear that the balance of evidence now favours the formula $Cl_2,6H_2O$ for this hydrate.

Tammann and Krige gave for the vapour pressure of chlorine hydrate the equation $t = 49{\cdot}0\ (\log p + 0{\cdot}4707)$, where t is in °C. and p in kg./sq.cm.[19]

Von Stackelberg determined the heat of formation of chlorine hydrate directly, by causing chlorine to react with hydrate-saturated cold water, and obtained the value 16900 g.-cal./mole, notably higher than that calculated from vapour pressure data. He also, by means of an *X*-ray powder photograph, found the lattice constant of the hydrate to be 11·98 ± 0·05 A.; the unit cell contains 8 chlorine molecules and they are free to rotate. The density corresponding to these *X*-ray data is 1·37 ± 0·02 g./c.c. (cf. 1·29 ± 0·02 obtained pyknometrically). The same author calculated that the heat of formation of the hydrate from ice and solid chlorine would be only 500 g.-cal./mole.[17]

Heat of Solution of Chlorine in Water.

From measurements of the heat of reaction of gaseous chlorine with aqueous alkali, Neumann and Müller calculated that the heat evolved in the reaction $Cl_2(gas) + aq. \rightarrow H^+aq. + Cl^-aq. + HOClaq.$ is 0·22 kg.-cal./mole.[20] From this and other available data, Roth estimated that if there were no hydrolysis the heat evolved would be about 6·9 kg.-cal./mole.[21] The actual observed heat of solution varies between these two values (Mellor, II, 74).

Liebhafsky noted that application of the Arrhenius equation to the solubility curve of chlorine indicates a varying heat of solution between 0° and 50°C. (even after allowing for varying hydrolysis); this he showed could be accounted for semi-quantitatively by assuming a varying degree of hydration of the chlorine molecules.[62]

The diffusion coefficient of chlorine in water at 25°C. was reported to be 1·16 g./sq.cm./day[22] (cf. Mellor, II, 74).

Constitution of Chlorine Water.

It has long been realized that chlorine water consists essentially of an equilibrium mixture of chlorine, water, hypochlorous acid and hydrochloric acid, the last existing almost entirely in the form of its ions H^+ and Cl^- (Mellor, II, 76). Table XX summarises recent values for the equilibrium constant

$$K = \frac{[H^+][Cl^-][HOCl]}{[Cl_2]} \text{ (all concentrations in moles per litre).}$$

TABLE XX. - HYDROLYSIS CONSTANT OF CHLORINE IN WATER

Author	Date	Temp. °C.	Values of $10^4 \times K$	Method
Roth[21]	1929	0	1·5 – 1·6	Cryoscopic
Whitney & Vivian[3]	1941	10	1·28	Solubility of the gas
		15	2·27	
		20	2·44	
		25	3·48	
Connick[23]	1947	0	1·45	Recalculation of Jakowkin's results
		12·8	2·88	
		25	4·47	
		35	5·68	
Hagisawa[24]	1941–2	25	2·09	pH measurements
cf. Jakowkin[7]	1899	0	1·56	Conductivity; also partition between water and CCl_4
		15	3·16	
		25	4·48	

The maximum conversion of chlorine into (free) hypochlorous acid occurs[25] when the pH is in the region 5 – 6.

It has been stated that, at higher temperatures, the equilibrium $3H_2O + 3Cl_2 \rightleftharpoons HClO_3 + 5HCl$ becomes important, and that an equilibrium constant $K = [H^+]^6[Cl^-]^5[ClO_3^-]/[Cl_2]^3$ could be determined by heating chlorine water, with manganous chloride as catalyst, in completely filled sealed tubes at 91°C. The value found for K was $4·3 \times 10^{-7}$ (the two acids were assumed to be only 77% dissociated), and for the free-energy change $\Delta G = 10{,}600$ g.-cal./mole.[41] In view of the high powers of $[H^+]$ and $[Cl^-]$ in the expression for K, these results would seem of doubtful value.

It is agreed (if one observation[26] is excluded) that the hydrolysis $Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl$ is a very rapid reaction. Shilov and Solodushenkov measured the reaction rate by a streaming method in which a concentrated chlorine solution was rapidly mixed with water, and caused to flow at high speed past successive pairs of electrodes for measurement of the conductivity, the progressive formation of H^+ and Cl^- ions being thus estimated. When chlorine water of initially 0·044 – 0·064 molar concentration was diluted to 0·006 – 0·024 M., it was found that the conductivity became constant in 1 sec. at about 1°C., and in 0·2 – 0·3 sec. at 17·6°,[27](previous work by Shilov and Kupinskaya had indicated that the reaction needed 1 – 2 min. for completion.[28] The first-order velocity constant of the hydrolysis was calculated to be 105 min.$^{-1}$ at 1° and 540 min.$^{-1}$ at 17·6°, the velocity constant of the reverse reaction at 1° being 6·7 x 10^5 (presumably expressed in mole^{-2} l.^{2} min.$^{-1}$). These velocity constants were confirmed by measurements of the rate of reaction between hypochlorous acid and phenol, which reaction requires the reversal of the hydrolysis as an intermediate step. To observe the reversal of the hydrolysis directly, a 0·0169 molar solution of hypochlorous acid was caused to react with 0·0225 M-hydrochloric acid by the streaming method at 3°C.: the conductivity became constant in about 0·5 sec.[27,29]

Since the hydrolysis velocity 'constants' found in this way diminished with time, Morris suggested that the results could best be interpreted by assuming that chlorine reacts with hydroxyl ion rather than with water ($Cl_2 + OH^- \rightleftharpoons HOCl + Cl^-$), and he derived velocity constants and ΔG values for this latter reaction.[30] Shilov and Solodushenkov rejected this mechanism because it could not be reconciled with their later, more accurate, experiments.[31]

Another worker calculated the velocities of the hydrolytic and reverse reactions from measurements of the rate of oxidation of arsenious acid by chlorine in aqueous solution at 25°. His values were for the hydrolysis rate constant 0·2073 and for the reverse rate constant 4·55 x 10^{-4}. As the units in which these constants are expressed were unspecified, it is not possible to compare his results with those of the Russian workers.[22]

Light Absorption by Chlorine Water.

Several workers have measured the extinction coefficients of chlorine water and found, after the effect of hydrolysis is allowed for, that the coefficients for dissolved chlorine are nearly the same as those of the gas.[32-34] According to Ferguson et al., this is true only down to 350 mμ, below which the dissolved chlorine absorbs more strongly than the gas ($\log \alpha = 1{\cdot}9$ at 320 mμ, 1·2 at 270 mμ and 2·0 at 220 mμ). Also, in 4 – 10 M-hydrochloric acid, chlorine shows an intense absorption band below 290 mμ. Ferguson et al. attributed this to the formation of complexes such as $Cl_2.OH^-$ or $HCl_2.OH$ (in water) and Cl_3^- (in hydrochloric acid – see below).[33] (See also page 349).

Photolysis of Chlorine Water.

Several studies of the reactions occurring in chlorine water on exposure to light have been made by Allmand and collaborators. They found that chloric acid and oxygen are formed, but not perchloric acid or hydrogen peroxide (cf. Mellor,II, 81). The conversion to chloric acid was 61 – 64% if the reaction was carried almost to completion, but was less if the reaction was interrupted at an early stage (e.g. 45·6% conversion to chloric acid for 14·5% decomposition, and 29·1% for 10·8% decomposition). The presence of a small concentration of added hydrochloric acid, up to 0·06 N., possibly increased the yield of chloric acid, but larger amounts definitely diminished it, e.g. at 0·340 N-HCl the yield was 24·0% (for 78% decomposition), and at 1·91 N-HCl the yield was only 1·9% (for 75% decomposition). The yield of chloric acid was lowered slightly by adding alkali-metal chlorides, but the presence of lithium sulphate increased it.

Corresponding to the absorption spectrum, the decomposition is brought about by light of all wave-lengths in the range 313 – 436 mμ (at least), the quantum yield increasing towards the ultra-violet. In their earlier work, Allmand et al. found quantum yields (expressed as molecules of chlorine or hypochlorous acid reacting per quantum absorbed) up to 2·1 for 0·5 molar solutions at 365 mμ and room temperature (at 46% decomposition), but in their latest work the highest values found at 365 mμ were 0·84 – 0·99 for 0·021 – 0·039 M-solutions, at 10 – 25% decomposition. Quantum yields obtained at 436 mμ and 313 mμ were respectively 0·41 (7% decomposition) and 1·94 (11% decomposition). The quantum yields diminished progressively with addition of hydrochloric acid, and were also somewhat reduced by the presence of alkali-metal chlorides. The temperature coefficient in the range 20 – 30°C. varied between 1·11 and 1·46 according to the wave-length.

The same authors also investigated the photolysis of hypochlorous acid solutions of pH 1·9 – 8·1 and of sodium hypochlorite solutions of still higher pH. The quantum yield for the decomposition was highest at pH 7·5, where a value of 1·94 in light of wave-length 365 mμ was obtained (for 11% decomposition). (See also page 514).

In their latest paper, the mechanism proposed for the first steps in the photolysis of chlorine water was (1) $Cl_2 + h\nu \rightarrow 2Cl$, (2) $Cl + H_2O \rightarrow H^+ + Cl^- + OH$, (3) $OH + Cl_2 \rightarrow ClO + H^+ + Cl^-$. It was suggested that, in dilute solutions with a low free-radical concentration, the ClO radical then reacts thus: (4) $ClO + Cl_2 + H_2O \rightarrow O_2 + 2H^+ + 2Cl^- + Cl$, (5) $Cl + Cl_2 + H_2O \rightarrow 2H^+ + 2Cl^- + ClO$, a slow chain-reaction which would account for the delayed evolution of oxygen observed after irradiation is discontinued. For higher radical concentrations, the reactions suggested were: (8) $ClO + OH \rightarrow H^+ + Cl^- + O_2$, or (9) $2ClO + H_2O \rightarrow 2H^+ + Cl^- + ClO_3^-$ (more chloric acid is produced in concentrated solutions). Another possibility is (10) $ClO + H_2O \rightarrow HO_2 + H^+ + Cl^-$, (11) $HO_2 + ClO \rightarrow H^+ + ClO_3^-$, Reasons given for the low quantum yields found in spite of these chain reactions were (*a*) the recombination of some of the pairs of chlorine atoms formed initially in (1), and (*b*) the endothermicity, –8 kg.-cal./mole, of reaction (2). The retarding effect of hydrochloric acid was attributed to a reaction $H^+ + Cl^- + OH \rightarrow H_2O + Cl$, and that of alkali chlorides to a reaction $Cl^- + OH \rightarrow Cl + OH^-$. It was suggested that the preferential formation of oxygen rather than chloric acid in the initial stages is due to the presence then of more hypochlorous acid: (*a*) $OH + HClO \rightarrow H_2O_2 + Cl$, (*b*) $H_2O_2 + HClO \rightarrow H_2O + H^+ + Cl^- + O_2$ or $H_2O_2 + Cl_2 \rightarrow 2H^+ + 2Cl^- + O_2$.[32,35,36] It appears that further work would be needed to establish these mechanisms quantitatively.

It has been reported that the decomposition of chlorine water in diffuse daylight (and possibly also in the dark) is accelerated by the presence of calcium or ferric chloride, or of magnesium sulphate, or of manganese dioxide.[37] Buchanan and Dodge found that residual chlorine in sterilized water was most readily lost when the wave-length of light irradiating it was between 250 and 300 mμ,[38] but here there may have been an effect due to the presence of organic matter.

Sanyal and Dhar found that the electrical conductivity of a weak solution of chlorine water, kept in the dark, showed a steady increase from the time of preparation. The conductivity of a strong solution remained constant.[39]

Solubility of Chlorine in Acid and Saline Solutions. The Cl_3^- ion.

Sherrill and Izard measured the solubility and activity coefficient of chlorine in aqueous solutions of acids and salts at 25°C. Table XXI gives some of their results, adjusted to a chlorine partial pressure of 760 mm. The activity coefficients given are the ratio of the concentration of unhydrolysed chlorine, in a saturated solution in pure water, to the same concentration in the acid or salt solution concerned. The solubilities quoted however, refer to the total amount of chlorine dissolved, expressed as molality (moles per 1000 g. water).

TABLE XXI. - SOLUBILITY AND ACTIVITY COEFFICIENTS OF CHLORINE IN CERTAIN AQUEOUS SOLUTIONS

	In Aqueous Sulphuric Acid								
Molality of H_2SO_4	0	0·500	1·024	1·969	3·009	3·993	4·990		
Cl_2 solubility, molal	0·0923	0·0627	0·0562	0·0498	0·0455	0·0428	0·0407		
Activity coefficient	1·000	1·097	1·165	1·270	1·34	1·39	1·45		
	In Hydrochloric Acid								
Molality of HCl	0·010	0·100	0·200	0·496	1·019	1·991	2·990	3·987	5·180
Cl_2 solubility, molal	0·0862	0·0634	0·0619	0·0630	0·0665	0·0737	0·0824	0·0914	0·1004
Activity coefficient	—	—	—	1·027	1·052	1·095	1·138	1·180	1·228
	In Aqueous Sodium Chloride								
Molality of NaCl	0·501	0·998	2·991	3·989	4·989				
Cl_2 solubility, molal	0·0658	0·0580	0·0416	0·0360	0·0309				
Activity coefficient	1·151	1·319	2·318	3·075	4·076				

With potassium chloride solutions it was found that the chlorine solubility was rather greater, and with barium chloride solutions rather less, than with sodium chloride solutions of the same molality. It is to be noted that small concentrations of hydrogen chloride diminished the solubility, owing to reversal of hydrolysis, but that larger concentrations increased it. Sherrill and Izard agreed with earlier work (Mellor, II, 83) in ascribing this solubility increase to the formation of trichloride ion: $Cl_2 + Cl^- \rightleftharpoons Cl_3^-$. The trichloride ion is presumably also formed in alkali chloride solutions, but there its influence on solubility is offset by the salting-out effect, which (as shown by the activity co-efficients) is much higher than in hydrochloric acid solutions.[1,40]

By making certain assumptions concerning relative salting-out effects on oxygen and chlorine in solutions of acids and salts, and assuming that Jakowkin's hydrolysis constant was still valid, the same authors were able to derive values for the trichloride-ion concentrations and hence for the equilibrium constant $K = \frac{\alpha_{Cl_3^-}\,[Cl_3^-]}{\alpha_{Cl^-}\,[Cl^-]}\,\frac{1}{p_{Cl_2}}$, where α denotes an activity coefficient. If $\alpha_{Cl_3^-}$ were taken equal to α_{Cl^-}, and $p_{Cl_2} = 1$ atm., the value found for K in hydrochloric acid solutions was about 0·01, but K was considerably less in concentrated solutions of alkali metal chlorides. With $K = 0{\cdot}01$, ΔG for the reaction $Cl_2(\text{gas}) + Cl^-(\text{aq.}) \rightarrow Cl_3^-(\text{aq.}) = -2730$ g.-cal./mole, and for the reaction $\frac{1}{2}H_2(\text{gas}) + \frac{3}{2}Cl_2(\text{gas}) \rightarrow H^+(\text{aq.}) + Cl_3^-(\text{aq.})$ $\Delta G = -28637$ g.-cal. per mole of HCl_3.

Kiss and Urmánczy similarly measured the solubility of chlorine in a number of chloride, sulphate and nitrate solutions. Their results, referring as before to total chlorine dissolved at 25°/1 atm., are shown in Fig. 4. The agreement with the results of Sherrill and Izard for sodium and potassium chloride solutions is very close when due allowance is made for the different methods of expressing concentrations. It is to be noted that the curves for sulphate solutions show initially an increase in the chlorine solubility. By assuming that the salting-out coefficients were the same as previously found with iodine in corresponding salt solutions, Kiss and Urmanczy calculated hydrolysis and trichloride-ion equilibrium-constants which varied in a complex manner with the nature and concentration of the salt. Their values for $K = [Cl\ ][Cl^-]/[Cl_3^-]$ were much higher for potassium and sodium chloride solutions

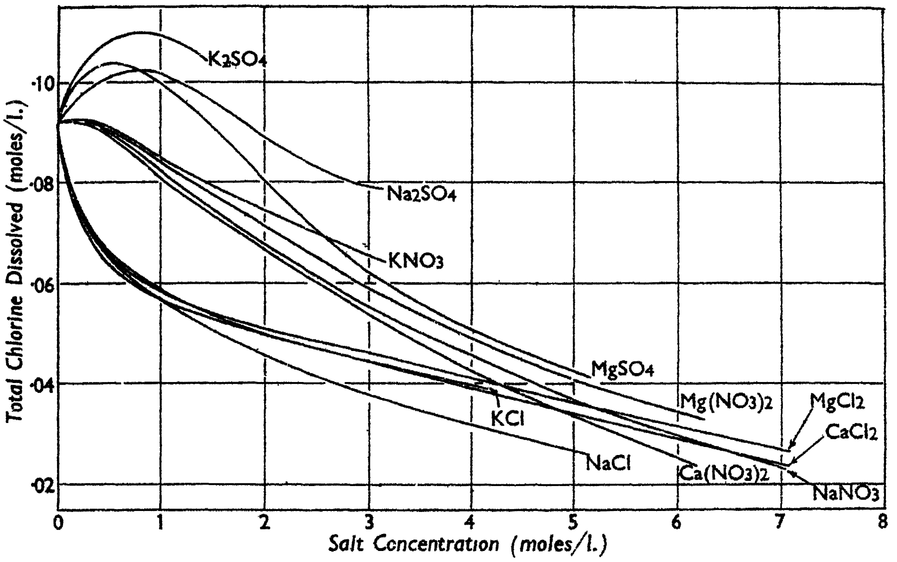

Fig. 4. SOLUBILITY OF CHLORINE IN AQUEOUS SALT SOLUTION

than those of Sherrill and Izard expressed on the same basis. By extrapolation, they found[2] that for chlorine in pure water $K = 4{\cdot}00$, corresponding to a concentration of $Cl_3^- = 0{\cdot}00047$ mole/l., against 0·0609 for (Cl_2) and 0·0306 each for HOCl, H^+ and Cl^-. Expressed in this way Sherrill and Izard's constant would have a value about 6.

Earlier work by Oliveri-Mandalà[42] gave the following values for the solubility of chlorine in sodium chloride solutions (as corrected by Seidel),[43] for 20°C. and a (? total) pressure of 762 mm.:

NaCl, moles/l.	0	0·777	1·323	1·965	3·159	3·597
Total Cl_2, moles/l.	0·0953	0·0705	0·0594	0·0496	0·0373	0·0321

The same author found that, in hydrochloric acid solutions at 20°/760·5 mm., the chlorine solubility varied from 0·1010 to 0·1243 molar as the hydrochloric acid concentration was varied from 1·155 to 4·101 molar.[42] The trend of these results was the same as those of the later workers.

Simple salts of the trichloride ion have not been isolated, but the tetraethylammonium salt $[(C_2H_5)_4N]^+Cl_3^-$, m.p. 42–45°, has been prepared. This is stable in a sealed vessel, but rapidly loses chlorine in air.[44]

Solutions of Chlorine in Non-aqueous Media.

Table XXII gives the values found by Taylor and Hildebrand[45] for the solubility of chlorine in various solvents. These results show only small deviations from Raoult's law, i.e. the solutions are nearly ideal.

Some not very exact measurements by other workers gave, for the ratio of the chlorine concentrations in the vapour and liquid phases in the chlorine-carbon tetrachloride system at 19°C., the value 0·031 ± 0·003.[46]

Blair and Yost measured the partial pressure of chlorine above dilute solutions in carbon tetrachloride at 25°. The values of the Henry's law constant (i.e. ratio of the chlorine partial pressure in mm. to the chlorine mole fraction in solution), over the mole-fraction range 0·00394–0·01391, varied between 4600 and 5280 with a mean value of 4960. Thermodynamic quantities

Refs. p. 371

TABLE XXII. - SOLUBILITY OF CHLORINE IN VARIOUS LIQUIDS

Solvent	Temp. °C.	Partial pressure of Cl_2, mm.	Solubility g.Cl_2/g. solution	Mole % Cl_2, calc. to 1 atm. Cl_2
n-Heptane	0	750	0·2036	27.0
$SiCl_4$	0	681	0·131	28·8
CCl_4	0	729	0·156	29·8
CCl_4	19	680	0·0848	18·7
CCl_4	40	557	0·0433	12·15
$CH_2Br.CH_2Br$	20	752	0·0813	19·2
$CH_2Br.CH_2Br$	40	736	0·0469	11·9

calculated for the formation of the solutions were: $\Delta G^\circ_{298} = -110$ g.-cal./mole, $\Delta H^\circ_{298} = -3720$ g.-cal./mole, $\Delta S^\circ = 37{\cdot}1$ entropy units.[47]

Values for the density and viscosity of dilute solutions of chlorine in carbon tetrachloride have been reported.[48]

Semb found the following values for the solubility of chlorine in heptane at a total pressure of 1 atm. (cf. above):

Temperature, °C.	−19·0	−11·0	0	11	20	30	40	60	76	77	85
Solubility (as g. Cl_2/100 c.c. soln.)	32·9	25·9	17·9	12·0	10·1	7·7	5·4	3·17	2·25	1·79	1·65

The results were somewhat affected by the onset of reaction between chlorine and the solvent.[49]

The freezing-points of the system chlorine/carbon tetrachloride were measured by Biltz and Meinecke, who found a eutectic of m.p. −114·5°C. at 86 − 87 atomic-% of chlorine, but no evidence of compound formation.[50] Wheat and Browne, however, found clear indication of five compounds CCl_4,nCl_2, where $n = \frac{1}{2}$, 1, 2, 3 or 4 (m.p. ranging from −67° to −115·5°), and there were six corresponding eutectics; they supposed that the chlorine atoms of the carbon tetrachloride molecule are each capable of donating an electron pair to an atom of a chlorine molecule: $R-Cl \rightarrow Cl-Cl$.[51]

These authors similarly obtained evidence of compound formation between chlorine and chloroform, methylene chloride, methyl chloride, and hydrogen chloride.[52,53]

Other systems for which data are available are those of chlorine with stannic chloride, titanium tetrachloride, silicon tetrachloride, or arsenic trichloride,[50] with phosphorus or antimony chlorides,[54] with phosphorus oxychloride,[55] with carbon dioxide,[56] with phosgene,[57] with boron chloride,[58] with ethylene oxide[59] and with iodine and bromine (see page 476). For further information on these, the reader is referred to later Supplements dealing with the elements concerned.

Liquid Chlorine as a Solvent.

Liquid chlorine has a low dielectric constant and the chlorine molecule in non-polar (see page 345); accordingly only substances with covalent molecules have appreciable solubility in liquid chlorine. Examples of such substances are the carbon compounds and hydrolysable chlorides just referred to, also diethyl ether, ethyl alcohol, acetone and ethyl acetate (the last four give conducting solutions if hydrogen chloride is present).[60] Butler and McIntosh tested a large number of anhydrous or hydrated metallic salts and found them all, including aluminium chloride, to be insoluble in liquid chlorine. They also found that sulphur, iodine trichloride, antimony trichloride and phosphorus pentachloride (cf. above), antimony and chromium sesquioxides, selenium dioxide and boric acid are insoluble. Stannic chloride becomes insoluble when hydrated. The constant for the elevation of the b.p. of chlorine by solutes is 1·73.[61]

The following values have been reported for the depression of the f.p. of chlorine by 0·01 mole fraction of the solutes named:[45]

	°C.		°C.		°C.
Acetone	0·190	Stannic chloride	0·208	Toluene	0·215
Ethyl acetate	0·199	Carbon tetrachloride	0·210	Chloroform	0·222
Diethyl ether	0·204				

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THE CHEMICAL PROPERTIES OF CHLORINE

Reactions of Chlorine with Hydrogen, Oxygen, Water, Hydrogen Peroxide and other Halogens.

It has been reported that the reaction between hydrogen and chlorine, when they are caused to flow through a tube (in the absence of light or catalysts) first becomes appreciable above 200°C.[1] With a static system, however, measurable rates of reaction have been observed in 'Pyrex' bulbs at 184°.[2]

A catalyzed reaction can be brought about at lower temperatures by passing the gases through strong solutions of the chlorides of aluminium, magnesium, zinc or tin; in the most favourable case, about 70% conversion to hydrogen chloride was obtained by passing the gases through 40% aluminium chloride solution at 130°.[3,4] Complete, non-explosive conversion has been obtained by passing the gases over quartz, coated with magnesium chloride, at 300°. With calcium chloride in place of magnesium chloride, the temperature required was 305°, with aluminium chloride 350°, and with quartz alone 380°. The chlorides were probably partly or wholly hydrolyzed as it was found necessary for a molecule of water to be present for each molecule of hydrogen chloride produced.[4,5] Explosive combination of hydrogen and chlorine can be catalyzed at room temperature by contact with yellow mercuric oxide.[6]

The slow, non-catalyzed thermal combination of hydrogen and chlorine has many features in common with the photochemical reaction (see page 391) including an obvious chain character and marked inhibition by oxygen. It is believed that the reaction is propagated by alternation in the gas phase of the reactions $Cl + H_2 \rightarrow HCl + H$ and $H + Cl_2 \rightarrow HCl + Cl$, the initial chlorine atoms being formed by dissociation of chlorine molecules on the vessel walls and the chains terminated by recombination of chlorine atoms also on the walls.[7,8,9] The evidence for the heterogeneous dissociation and recombination of the chlorine is that an increase of the surface/volume ratio of the reaction vessel has no effect on the reaction rate unless oxygen is present; in the latter case chains are destroyed mainly by the reaction $H + O_2 \rightarrow HO_2$ in the gas phase, and an increase in the vessel surface then gives an increase in the rate owing to increased formation of chlorine atoms.[7] In a clean 'Pyrex' bulb the rate equation is:

$$\frac{d\frac{1}{2}[HCl]}{dt} = \frac{k[H_2]^2[Cl_2]}{\frac{1}{2}[HCl]}, \text{ becoming } \frac{d\frac{1}{2}[HCl]}{dt} = k[H_2][Cl_2]^{\frac{1}{2}}$$

in a bulb coated with potassium chloride.[2] A recent review[8] gives for the reaction in presence of oxygen the equation:

$$\frac{d[HCl]}{dt} = \frac{k'\ [H_2][Cl_2]^2}{m'[Cl_2] + [O_2][(H_2) + k''(Cl_2)]}$$

Studies have also been made of the slow combination of hydrogen and chlorine at room temperature, initiated by the introduction of hydrogen atoms,[10,11] chlorine atoms,[12] ionized nitrogen,[13] alpha-particles,[14] or *X*-rays.[15] Except for the mode of initiation, the phenomena observed resemble closely those of the photochemical reaction which is the subject of a later section (page 391).

The minimum pressure for the inflammation of hydrogen-chlorine mixtures is related to the temperature by the equation $\log (P_m/T) = A/T + B$, where P_m is in cm., $A = 2600-2900$, T is in °K., and B is a quantity having a value depending on the composition of the mixture and diminishing with increasing size of the vessel. Thus at 623°K. in a particular vessel it was found that $P_m = 22$ cm. at 35% chlorine, diminishing to 6 cm. at 66% chlorine and rising again to 22 cm. at 92% chlorine.[16]

The limiting compositions for the explosion of hydrogen-chlorine mixtures at atmospheric pressure have been given by various authors as shown in Table XXIII.

TABLE XXIII. - EXPLOSION LIMITS FOR HYDROGEN–CHLORINE MIXTURES

Hydrogen content of explosive mixtures, vol. %	Type of vessel	Mode of ignition	Author	Date
8·1–85·7	Glass tube, diam. > 1 cm.	Spark	Matthieu[17]	1917
7 –83*	Glass bulb	Spark	Weissweiler[18]	1936
6 –84	Bomb, 1 l.	Spark		
10·4–83·9	Burette	Spark	Lindeijer[19]	1937
5·5–86	Cylinder, vol. ½ l., diam. 4 cm.	Spark	Kunin & Serdyukov[20]	1946
7 –89		Hot Pt wire		

* Development of pressure, without a flame or report, was noted for 3·5–7% and 83–97% hydrogen.

The above figures may be compared with the range 9·8–52·8% of hydrogen found for photo-ignition by the light of burning magnesium wire.[17] Other work on photo-ignition is described later (see page 395).

The explosion limits found are liable to vary with the number of sparks passed or the rate of heating of the ignition wire. The temperature to which the latter had to be heated varied between 350° and 227° for 7–18% hydrogen, and between 780° and 1030° for 88–89% hydrogen.[20]

Attempts to ignite hydrogen–chlorine mixtures by means of 35–45 kV. electrons have been unsuccessful.[21]

The flame-velocity in hydrogen–chlorine mixtures of various compositions has been determined by burning a stream of the gases at a specially shaped nozzle. The values found are given in Table XXIV.

TABLE XXIV. - FLAME VELOCITIES IN IGNITED HYDROGEN–CHLORINE MIXTURES

Chlorine content, as a fraction of the stoicheiometric ratio.	0·45	0·49	0·45	0·59	0·64	0·73	0·77
Flame speed, cm./sec.	350	380	410	410	390	330	300

The fact that the maximum flame speed does not correspond with the stoicheiometric proportion of reactants is attributed to the presence of atoms, especially hydrogen atoms, in the flame.[22] In a later paper the same author gives the following results, which despite minor differences confirm and illustrate these conclusions.[23]

TABLE XXV. - FLAME SPEEDS, TEMPERATURES, AND ATOM CONTENTS FOR HYDROGEN–CHLORINE MIXTURES

Chlorine content; fraction of stoicheiometric ratio	Flame speed cm./sec.	Maximum flame temperature, °K. (calc.)	Estimated atom contents in hottest zone	
			%H	%Cl
0·55	360	2260	0·38	0·67
0·68	405	2402	0·75	2·08
1·0	350	2501	0·49	8·13

Explosion limits have also been determined for mixtures of hydrogen and chlorine with various other gases as shown in the following summary:-

Mixture	Principal Findings	Author
H_2-Cl_2-N_2	70% N_2 prevents explosion at any H_2:Cl_2 ratio. See Fig. 5.	Lindeijer[19] Kunin and Serdyukov[20]
H_2-Cl_2-O_2	See Fig. 6. 2% deviation from Le Chatelier straight-line formula at low H_2 and Cl_2 contents.	Lindeijer[19]
H_2-Cl_2-CO	69% CO prevents explosion at any H_2:Cl_2 ratio. No $COCl_2$ formed.	Lindeijer[19]
H_2-Cl_2-N_2O*	N_2O has a similar action to N_2 and CO; some NO_2 formed.	Lindeijer[19]
H_2-Cl_2-NO	H_2 is combustible in all mixtures of Cl_2 and NO. Limited incombustible region if 10% N_2 present.	Jorissen[24]
H_2-Cl_2-HCl	70% HCl prevents explosion at any H_2:Cl_2 ratio. Large amounts of HCl tend to increase the minimum H_2:Cl_2 ratio required for explosion.	Kunin and Serdyukov[20]
H_2-Cl_2-HCl-CO_2	CO_2 has an inhibiting effect: small proportions of it increase the % H_2 and Cl_2 required for explosion.	Kunin and Serdyukov[20]
H_2-Cl_2-HCl-N_2	No explosions at >70% N_2. With hot-wire ignition, signs of inhibition by small amounts of N_2.	Kunin and Serdyukov[20]
H_2-Cl_2-HCl-O_2	O_2 reduces the proportions of H_2 and Cl_2 required for ignition, but small amounts of it have an inhibiting effect with hot-wire ignition.	Kunin and Serdyukov[20]

*The original paper refers to 'nitrous oxide', but gives the formula as NO; if nitric oxide was in fact used, the results differed from those of Jorissen.

For additional explosion-limit diagrams, reference should be made to the original papers.

The use of the hydrogen–chlorine reaction as a means of producing hydrogen chloride in quantity is described in the section on the preparation of hydrogen chloride (see page 402).

Oxygen is inert towards chlorine under all ordinary conditions, but chlorine monoxide and dioxide have been obtained by the action of monatomic oxygen on chlorine.[25] Also there is evidence that ClO radicals can have a transient existence after the irradiation of chlorine–oxygen mixtures by an extremely intense light-flash.[26] ClO radicals have also been detected spectroscopically during combustion of hydrogen in a mixture of 30% chlorine: 70% oxygen.[27]

Ozone undergoes a photosensitized decomposition when mixed with chlorine and irradiated with blue or near-ultraviolet light.[28,29] An interaction between chlorine and ozone also occurs in the dark, giving a measurable rate of ozone decomposition at 35°C., after an induction period has elapsed.[30,31] In both these reactions the formation of the unstable chlorine hexoxide, Cl_2O_6, has been detected[31,32,33] and, under irradiation by blue light, also the heptoxide, Cl_2O_7.[34] The greater part of the chlorine, however, remains unchanged when all the ozone has decomposed.[29] Numerous studies of the reaction kinetics

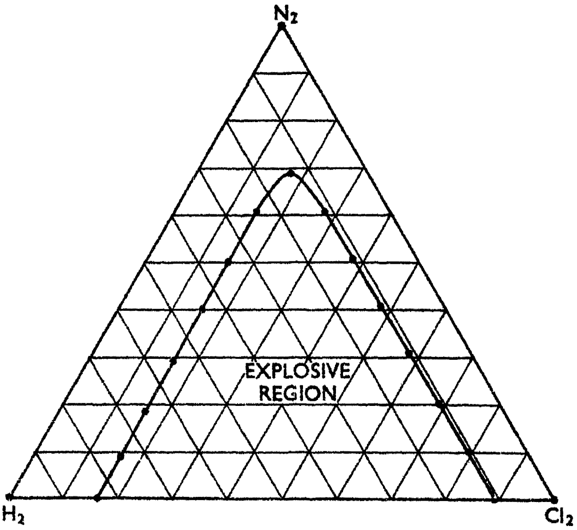

Fig. 5. EXPLOSION LIMITS FOR H_2-Cl_2-N_2 MIXTURES TAKEN FROM LINDEIJER[19]

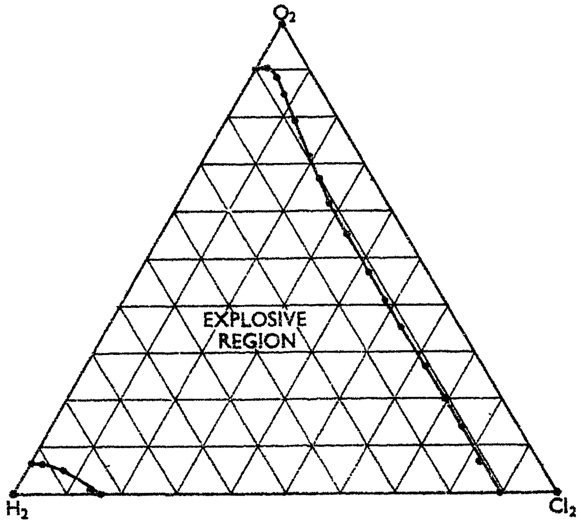

Fig. 6. EXPLOSION LIMITS FOR H_2-Cl_2-O_2 MIXTURES TAKEN FROM LINDEIJER[19]

have been made[10,31,35-37] but as the subject concerns the chemistry of ozone rather than of chlorine, the following will suffice as a typical example of the mechanisms proposed for the photo-sensitization:[35]

(1) $Cl_2 + h\nu \rightarrow 2Cl$

(2) $Cl + O_3 + M \rightarrow ClO_3^* + M$ (M is any third molecule; ClO_3^* is an excited radical)

$$\begin{aligned}&(3)\ ClO_3^* + O_3 \longrightarrow ClO_2 + O_2\\&(4)\ 2ClO_3 \rightarrow Cl_2 + 3O_2\\&(5)\ 2ClO_3 \rightarrow Cl_2O_6\end{aligned}$$

This gives an overall quantum yield of 2 for the ozone decomposition, as found by some experimenters, but does not take into account the subsequent onset of rapid thermal reaction.

'Active' chlorine (see page 382) has been reported to react with ozone to form chlorine monoxide.[38]

The reaction of water with chlorine in the liquid phase has already been discussed in the sub-section on solutions (see page 365). For the gas-phase equilibrium, $2Cl_2 + 2H_2O \rightleftharpoons 4HCl + O_2$, some values for the enthalpy and free-energy changes and the equilibrium constant[39] are given in Table XXVI.

TABLE XXVI. - THERMODYNAMIC VALUES FOR THE REACTION $2Cl_2 + 2H_2O \rightleftharpoons 4HCl + O_2$.

T °K.	ΔH (g.-cal.)	$\Delta G_0/T$ (g.-cal/deg.)	log K
298·16	27,345	60·809	13·290
400	27,566	37·363	8·166
600	27,838	14·277	3·120
700	27,926	7·635	1·669
800	28,008	2·632	0·575
900	28,094	−1·275	−0·279
1000	28,181	−4·413	−0·965
1100	28,233	−6·989	−1·527
1200	28,386	−9·141	−1·998
1600	28,792	−15·124	−3·305
2000	29,136	−18·765	−4·101

In the above table, $K = \dfrac{(n_{H_2O})^2(n_{Cl_2})^2}{(n_{HCl})^4(n_{O_2})} \cdot K_\nu \cdot \dfrac{\Sigma n}{\pi}$ where n_{H_2O}, n_{Cl_2} etc. are the numbers of moles of each species in the system, Σn is the total number of moles (including inert gases), π is the total pressure in atmospheres, and K_ν is a factor depending on the fugacity coefficients; K_ν is equal to unity at atmospheric pressure. The values for K agree closely with those determined experimentally in the range 680 – 920 °K.,[40,41] and also with those of an earlier calculation covering the range 600 – 1000° K.[42] Another paper gives for ΔH_{298} 25,440 g.-cal. and for ΔG^0_{298} 16,760 g.-cal. ($\Delta G^0/T = 56{\cdot}21$ g.-cal./deg. taking $T = 298{\cdot}16$° K.),[43] but these figures are not consistent with the values selected for the enthalpy and free energy of the components in the latest tables of the U.S. National Bureau of Standards.[44]

The reaction between steam and chlorine, in presence of activated charcoal at 800 – 1000°C., has been proposed as a means of removing free chlorine from gaseous mixtures containing it, but elsewhere it is stated that carbon is oxidized to carbon dioxide under such conditions.[45,46] Similarly it is reported that other reducing substances exposed to a reacting mixture of steam and chlorine are oxidized – iron to ferric oxide together with some ferric chloride, toluene to benzoic acid etc.[46]

No net photochemical reaction, in visible or ultra-violet light, can be detected between chlorine and water vapour,[47] although one observer noted the appearance of (unidentified) liquid droplets which vanished when illumination was discontinued.[48]

Hydrogen peroxide with chlorine undergoes a reaction $H_2O_2 + Cl_2 = O_2 + 2HCl$. The kinetics of this reaction have been studied by numerous workers, and the reaction has been held to be essentially one between the peroxide and hypochlorous acid formed by hydrolysis of the chlorine.[49-54] The most recent study, however, gives mechanisms which vary with the hydrochloric acid content of the liquid. Thus at [HCl] = 10^{-4}M. or more, the mechanism given is:

$$(1)\ H_2O_2 + Cl_2 \underset{k_b}{\overset{k_a}{\rightleftharpoons}} H^+ + Cl^- + HOOCl$$

$$(2)\ HOOCl \xrightarrow{k_a} O_2 + H^+ + Cl^-$$

and the corresponding rate equation is $-\dfrac{d[H_2O_2]}{dt} = \dfrac{k_a}{k_b}\dfrac{k_c[H_2O_2][Cl_2]}{[H^+][Cl^-]+k_c}$. In the region above [HCl] = 1M., the decomposition of HOOCl is the rate-determining step, whereas at lower acidity the slow reaction of peroxide with chlorine controls the rate. For values of [HCl] < 10^{-4}M., where nearly all the chlorine is hydrolyzed, the mechanism given is:

$$(1)\ HOCl \rightleftharpoons H^+ + ClO^-$$

$$(2)\ ClO^- + H_2O_2 \longrightarrow H_2O + O_2 + Cl^-,$$

the latter being the rate-determining step, and the corresponding rate equation is $-\dfrac{d[H_2O_2]}{dt} = \dfrac{k[H_2O_2][HOCl]}{[H^+]}$. In the region where $[H^+][Cl^-] = 10^{-5}$ to 10^{-8} the rates become variable and difficult to interpret.[54]

When chlorine is passed into 100-vol. hydrogen peroxide mixed with a large excess of aqueous potassium hydroxide (280 g. per l.), the reaction which occurs is expressed by the equation $2KOH + H_2O_2 + Cl_2 = 2KCl + 2H_2O + O_2$. Under suitable conditions a red luminescence occurs during the reaction.[55,56]

The occurrence of any chemical reaction between bromine and chlorine was at one time thought to be very doubtful (Mellor, II, 114), despite indications of such a reaction obtained by early workers even as long ago as 1826.[57] The existence of the reversible reaction $Br_2 + Cl_2 \rightleftharpoons 2BrCl$ has, however, since been proved by observations of the changes of light absorption which take place when bromine vapour and chlorine are mixed.[58-60] In the dark at room temperature, equilibrium is attained only after many hours from the time of mixing, but the period is greatly reduced by the use of a freshly cleaned vessel or by irradiation with light of wavelength 365 mμ.[61] Equilibrium constants have been determined by various workers, and values about 0·11 are given for $K = [Br_2][Cl_2]/[BrCl]^2$, at room temperature.[58,61-65] The value of K rises slowly with temperature indicating that the forward reaction is slightly exothermic: values of 230 – 750 g.-cal./mol. are given for $-\Delta H$.

There is evidence also from a study of oxidation potentials that chlorine and bromine combine when in solution in 4 N- or 6 N-hydrochloric acid. The estimated equilibrium constant was $3{\cdot}2 \times 10^{-4}$, indicating more complete combination than in the gas phase.[66]

The high-temperature equilibrium (up to 473°C.) between iodine and chlorine has been studied and the value ΔG° for the reaction $\frac{1}{2}I_{2(gas)} + \frac{1}{2}Cl_{2(gas)} \rightarrow ICl_{(gas)}$ found to be $-3125 - 1{\cdot}36T$ g.-cal./mole (T in °K.).[67,68] The reaction between iodine and chlorine in carbon tetrachloride solution is reported to be accelerated by light and by traces of water; the reaction in presence of water has a large negative temperature coefficient.[68] An investigation of the solid and liquid phases in the system iodine – bromine – chlorine at 29·8°C. did not indicate the formation of any ternary I – Br – Cl compound.[69] The occurrence of a violent reaction between iodine and liquid chlorine has been reported.[180]

The phase diagram of the system hydrogen chloride/chlorine reveals the formation of the compounds H_2Cl_3 (congruent m.p. -115°C.) and H_2Cl_4 (congruent m.p. -121°).[70] Earlier workers found only a eutectic (73%HCl, m.p. -127°).[71]

Hydrogen iodide reacts very rapidly with chlorine in various organic solvents at temperatures down to -110°. A homogeneous bimolecular reaction mechanism has been proposed.[72]

The combination of fluorine and chlorine is described in an earlier section (see page 147).

Reactivity of Chlorine towards other Elements and their Compounds.

Details of the reactions of chlorine with elements and their compounds, other than those dealt with in the preceding paragraphs, will be given in the later volumes of this Supplement devoted to those elements. The following paragraphs are intended chiefly as examples giving an indication of the general reactivity of chlorine towards the remaining elements and their compounds (cf. Mellor, II, 92-96).

Sulphur dioxide combines slowly with chlorine in light, giving sulphuryl chloride; the reaction is catalyzed by a variety of ketones and other oxygen-containing organic compounds.[29,73,74] A dilute solution of hydrogen sulphide in anhydrous liquid hydrogen chloride reacts with chlorine at -100°, liberating sulphur.[75] Selenium and tellurium react readily at -80° with liquid chlorine, forming the tetrachlorides.[182]

Nitrogen passed with chlorine through an arc maintained between platinum-iridium electrodes yielded no trace of nitrogen chlorides.[76] Ammonium ions are said to be attacked by chlorine only after it has been converted into hypochlorous acid.[77] Reaction between nitric oxide and chlorine can be detected down to -180°C.; it is reported that this reaction gives rise to the compound $NOCl_2$ as well as nitrosyl chloride and that adsorption of the latter on the surface of the vessel can inhibit the reaction completely.[78-82] Nitrite ions react very rapidly and completely with chlorine at $pH = 6$ or less, but at higher pH values the reaction is slow and incomplete, the equilibrium depending on concentration, temperature and other factors.[83] Fuming nitric acid reacts slowly with chlorine at 15-18°C., forming chloric acid and nitrogen dioxide.[84]

Liquid chlorine at its b.p. reacts explosively with white phosphorus,[180] and inflammation occurs when a solution of chlorine in heptane is added to red phosphorus at 0°C.[85] Phosphine and phosphorus trichloride are reported not to react appreciably with chlorine at -20°, but phosphonium chloride reacts vigorously even at -100°, especially if chlorine is in excess, phosphorus pentachloride and other products being obtained.[75] Phosphorus tribromide reacts with chlorine to give the compounds $PClBr_2$ and $PClBr_4$.[86] The phosphorus nitrides P_3N_5 and P_4N_6 give with chlorine at 700° the chloronitride $(PNCl_2)_3$ and a little phosphorus pentachloride.[87] Arsenic undergoes only superficial attack by liquid chlorine at its b.p.,[180] but arsine reacts readily with chlorine down to -140°, forming reddish substances; also the arsenic chlorohydrides AsH_2Cl and $AsHCl_2$ are readily attacked.[75] A solution of chlorine in heptane is very rapidly decolorized by contact with antimony.[85] Stibine with chlorine liberates antimony, forming hydrogen chloride and also some antimony pentachloride.[75]

The formation of some carbon tetrachloride by passage of chlorine, mixed with sulphur dichloride, over active charcoal at 700-800°C. has been reported, but the effect was attributed to a chain of reactions involving sulphur chlorides, sulphur and carbon disulphide rather than to a direct reaction between chlorine and carbon.[181] The chemical action of chlorine on coal appears to be mainly due to combination of chlorine with the hydrogen and sulphur contained in the coal.[88,89] The kinetics of the thermal and photochemical reactions of carbon monoxide with chlorine, to form carbonyl chloride, have been intensively studied;[90-93] this reaction will be discussed in the chapter on carbon in a later volume. The reaction $CO + Cl_2 + H_2O \rightarrow CO_2 + HCl$, catalyzed by activated charcoal at temperatures above 350° F. (177° C.), has been proposed as a means of removing free chlorine from hydrogen gas (cf. page 377).[94] Chlorine has a marked inhibiting effect on the combustion of carbon monoxide with oxygen.[95]

As examples of the reactivity of hydrocarbons towards chlorine may be cited the explosive reaction of methane with chlorine over yellow mercuric oxide at room temperature, a similar reaction of ethylene with chlorine over mercurous oxide, mercuric oxide, or silver oxide (also over litharge at 100–120°), and the occurrence of an explosion of liquid chlorine and petrol at 21° in a steel cylinder.[6,97,98] Starch is partly degraded by chlorine.[99]

The evidence concerning the action of chlorine on silica is conflicting. It has been stated that amorphous silica reacts with chlorine in presence of carbon at 740°, but that a temperature of 1220° is required for quartz; the sequence of reactions is given as (1) $SiO_2 + 2Cl_2 \rightarrow SiCl_4 + O_2$, (2) $2C + O_2 \rightarrow 2CO$.[100,101] Another reaction is that fused quartz, silica gel, and amorphous silica all begin to react with chlorine alone at 900–950°.[102] It has been asserted that carbon does not affect the temperature required for the onset of reaction, but accelerates the reaction by preventing the establishment of an equilibrium between silicon, oxygen and chlorine.[103] Boron trioxide is reported to be inert to chlorine up to 900°.[104] Liquid chlorine has no action, even up to its critical temperature, on silicon, and it is also inert to boron.[182]

Alkali metal vapours and chlorine interact readily at a pressure of 10^{-3}mm. and 300° C., with formation of a luminous flame. These reactions have been the subject of many studies of reaction mechanism.[105-107]

A solution of chlorine in heptane has been reported to be decolorized after contact for some hours with lithium, sodium, copper, or lead, but not with bismuth. A saturated solution in the same solvent reacted with inflammation when added to copper powder at a temperature well below 0° C.[85] It may, perhaps, be presumed that light of wave-lengths absorbed by chlorine was excluded during these experiments.

Liquid chlorine at its b.p. acts on tin violently, with incandescence, and it also combines with aluminium, but copper, zinc and silver are merely coated with the corresponding chlorides.[180] At higher temperatures, in sealed tubes, it reacts with various metals as follows:[182]

Metal	Conditions of reaction	Product
Lead	Slight attack at room temp.	$PbCl_2$
Silver	Very slight attack at 80°	-
Platinum	Very slight attack at 90–100°	-
Gold	Attack at 80° is more severe than with Ag and Pt	$AuCl_3$
Chromium	Attacked at 80°, if water is present	$CrCl_3$ (hydrated)
Manganese	Attacked at 80°, if water is present	$MnCl_2$
Vanadium (powder)	Explosive reaction when temp. rises to 0°. Controllable by dilution with CCl_4	VCl_3

Temperatures found for the onset of vigorous reaction between dry chlorine gas and the following metals (degassed) are: calcium 460°, magnesium 340°, tin 25°, iron 280°.[108] Steel in sheet form has been observed to ignite after exposure for 30 min. to dry chlorine at 251°, and steel wool of the American grades 00, 0, and 2 ignites at 184°, 189° and 194° respectively.[109] Other workers report the ignition temperature of 'carbon steel' or of cast iron as 230–260°, that of aluminium as 200–230°, and that of copper as 320° (see page 385).[110] For the three metals copper, lead and silver, in the temperature region 15 – 644°, the velocity of reaction diminishes in the order named; the thickness of the chloride layer increases with time according to a parabolic law.[111,112,178]

The ready reaction of dry mercury with dry chlorine has been confirmed.[113] When chlorine at atmospheric pressure is passed over a mercury surface heated at 200 – 300°, a flame is formed which emits a continuous spectrum having a maximum intensity at 5600 – 6500 A.[114] The reaction between mercury vapour and an air/chlorine mixture at 20° was stated to be too rapid for kinetic measurements.[115]

Niobium in powder form reacts energetically with chlorine, forming the pentachloride.[116]

The corrosion of metals by chlorine, considered as a practical problem, is discussed later (see page 385).

Among the metallic oxides, silver and mercuric oxides react rapidly with chlorine at room temperature, whereas sodium monoxide, lithia and calcium oxide react only slowly. Chlorine monoxide is detected in the gaseous products of reaction between chlorine and mercuric or calcium oxide. With sodium monoxide, the solid product contains some sodium peroxide, chlorate and hypochlorite; the peroxide is formed also from barium monoxide.[117]

The temperatures given by several authors for the onset of reaction of chlorine with other oxides are quoted in Table XXVII.

TABLE XXVII. - TEMPERATURES REQUIRED FOR REACTION OF CHLORINE WITH METALLIC OXIDES

Oxide	Temperature required for detectable reaction °C.	Reference	Temperature[104] required for oxide to react at rate of 1% per hr. °C.
CuO	<100	118	-
BeO	600	103	1050
MgO	<427	119	-
CaO	18 – 23*	120	-
ZnO	<100	118	350
CdO	-	-	450 (cf. above)
Al_2O_3	800, >800, ~850	103,121,100	1200
TiO_2	>800	121	800
SnO	-	-	[readily at 550][122]
PbO	<100	-	-
V_2O_5	400	123	500
Nb_2O_4	200	124	-
Nb_2O_5	-	-	800
Cr_2O_3	600	100	-
MoO_3	400	100	500
WO_3	700	100,121	700
U_3O_8	-	-	900
MnO	<500	100	-
FeO	200	100	-
Fe_2O_3	400, ~525, 600	103,100,125	-
CoO	300	100	-
NiO	400	100	-

* Elsewhere it is stated that chlorine has only a 'superficial' action on anhydrous calcium oxide.[126]

With many of these oxides, the reaction is accelerated by the presence of carbon, e.g. with ferric oxide chlorination then takes place at temperatures from 125 – 350°, according to the temperature at which the oxide has been calcined.[121]

Usually the action of chlorine produces the chloride of the metal, but with tungsten and vanadium oxides the oxychlorides WO_2Cl_2 and $VOCl_3$ are formed, respectively.[121,125] An oxychloride has also been detected in the products of the reaction with alumina.[127]

For discussion of equilibria in the reactions between metallic oxides and chlorine, the reader is referred to the chapters in later Supplements which will deal with the relevant metals.

Heavy-metal sulphides (PbS, ZnS, Cu_2S, Ag_2S, FeS_2) are acted on by chlorine at lower temperatures than are the corresponding oxides.[118] It was observed that chlorine removed 95% of the sulphur from iron pyrites at 600°.[128] The sulphates of lead, zinc and copper react only slowly with chlorine below 700°.[118] The sulphates of barium, strontium, calcium and sodium are largely converted into the chlorides by heating at 850 – 1050° in a stream of chlorine; the reactions are more rapid in the presence of sodium chloride or of reducing agents.[129-132]

The carbonates of sodium and potassium react with chlorine according to the equation $2M_2CO_3 + 2Cl_2 = 4MCl + 2CO_2 + O_2$, perchlorates being formed as a by-product. The carbonates are the more reactive the lower is the temperature used in preparing them from the corresponding bicarbonates; the chlorination temperature may be as low as 150° for sodium carbonate and 200° for potassium carbonate. Lithium carbonate gives a small conversion to chloride at 300 – 500°, no perchlorate being formed.[133,134] Calcium carbonate slowly reacts to form the chloride at 600°.[135]

Among the reactions of chlorine with metallic halides, two values given for the equilibrium constant at 800°C. for the reaction $2KBr + Cl_2 \rightleftharpoons 2KCl + Br_2$ are respectively 303 and 273, i.e. the formation of chloride greatly predominates. High values are given also with sodium or lead as the cation concerned, but a lower value, 11·28, is reported with silver as the cation.[136,137] Gaseous chlorine passed over solid potassium bromide or iodide at 20° or 30° gives no reaction unless the gas contains a minimum partial pressure of water vapour, approximating to the vapour pressure of a saturated solution of the components.[133] Stannous fluoride reacts with chlorine with inflammation: $2SnF_2 + 2Cl_2 = SnF_4 + SnCl_4$.[122]

Hypochlorites of the alkali and alkaline-earth metals with chlorine are either decomposed in reactions of the type $MOCl + Cl_2 = MCl + Cl_2O$, or the chlorine catalyzes a reaction $3MOCl \rightarrow MClO_3 + 2MCl$.[139] A dilute solution of calcium chlorite treated with chlorine evolves chlorine dioxide: $2ClO_2^- + Cl_2 = 2Cl^- + ClO_2$.[140]

Silicates and spinels are reported to be more resistant to attack by chlorine than are the constituent oxides.[141] Silicates differ very much amongst themselves in their reactivity to chlorine – thus the metasilicates of sodium, magnesium, and especially lead, begin to react with chlorine at 15 – 50°, the reactions being more rapid in presence of water, and calcium metasilicate is attacked at 18 – 23°, whereas a temperature above 1000° is required for complete chlorination of the various oxides contained in serpentine.[120,142,143] Firebrick is attacked by chlorine at 1000° owing to loss of iron as ferric chloride.[144] The iron silicate mineral grünerite is attacked by chlorine at 350°.[100] Hydrated Portland cement reacts with chlorine, forming a hydrated calcium chloro-aluminate: the pressure exerted by the crystals of this compound causes the concrete to crack, and binding material may also be removed.[145] Certain quick-setting silicate cements, however, are resistant to chlorine up to 400°C. or more.[177]

Active Chlorine.

Chlorine which has been subjected to a silent electric discharge acquires and retains for a short time, e.g. more than 75 sec., an abnormal chemical reactivity. Thus it combines with ozone to produce chlorine monoxide and with sulphur and tellurium to form chlorides; it can initiate a chain reaction with hydrogen, and it is more reactive towards water, acetic acid, benzene, toluene and benzyl alcohol than is ordinary chlorine though it is allegedly less reactive towards ferrous sulphate. It has been stated that this active condition can be brought about also by irradiation with ultra-violet light, but another report is that the activity produced by electric discharge is not increased by irradiation of the gas during the discharge. A statement that the activity can be produced thermally is unconfirmed. Earlier it was thought that 'active' chlorine is an allotropic form of the element (it was found as long ago as 1905 that the active form is not ionized and that its density is sensibly the same as that of normal chlorine), but later workers have regarded the phenomena as due to the presence of small amounts of atomic chlorine, the properties of which are discussed below.[12,38,146-152]

Monatomic Chlorine and its Reversion to Molecular Chlorine.

It has been claimed that the conversion of chlorine to the monatomic state was as high as 43% when the gas was passed at 0·1 mm. pressure through a quartz Wood's tube fitted with water-cooled iron A.C. electrodes; the average life-period of the atoms was 3×10^{-3} sec. in the outlet tube.[150,151]

The reversion of chlorine atoms, produced by an electric discharge or photochemically, to the molecular state is a slow process in the gas phase; e.g. it is reported that only 1 in 10^8-10^9 collisions between pairs of atoms leads to combination.[153] Presumably it is this relatively slow combination which enables the transient properties of 'active' chlorine to be observed at ordinary pressures. Collisions with a solid surface are much more effective in bringing about the recombination: one estimate is that 2 in every 25 collisions with a quartz surface leads to union of the atoms.[157]

The relative catalytic effect of various solid surfaces for the recombination has been estimated from the heating effects when chlorine atoms impinge on the surfaces, and in this way it has been found that silver, silver chloride, copper, nickel, tin and gas carbon are particularly effective as catalysts. Silver and tin, but not nickel or aluminium, are attacked under these conditions. Catalysis of the recombination is shown also by red phosphorus, chromium sesquioxide, cobalt and fused calcium chloride, potassium chloride (with variable behaviour), and to a smaller extent by Pyrex glass, platinized glass and sodium chloride.[12,150,151] Carbon dioxide and hydrogen chloride activate the recombination on quartz and glass respectively.[154,155] Chlorine atoms have been observed to survive passage through a glass tube even though the temperature was much below the normal boiling-point of the liquid, but a claim to have passed them through a narrow copper tube to initiate a reaction between hydrogen and chlorine seems at variance with the high catalytic activity of copper,[12,156] unless it may be assumed that streamline flow greatly minimized contact between the gas and the walls of the tube.

Among substances which retard the combination of chlorine atoms, or poison surfaces which would otherwise catalyze it, are methane, chloroform and platinum chloride.[149,151] Oxygen has no effect on atomic chlorine, except perhaps under the extreme conditions following a very intense light flash, but it inhibits the formation of chlorine atoms if it is present before the electric discharge is applied.[26,151] Other substances reported to have no effect are hydrogen chloride (but see above and the reports of retardation, by the hydrogen chloride formed, of the photochemical combination of hydrogen and chlorine (see page 393), also carbon tetrachloride and phosgene. Ethylene gives with atomic chlorine an explosive compound which can be collected on a surface cooled in liquid air; the compound has possibly the free-radical formula $CH_2Cl.CH_2^-$.[154]

There is evidence from a study of the Budde effect that the recombination of chlorine atoms in the gas phase occurs by the mechanism $Cl + Cl_2 + M \rightarrow Cl_3 + M$, followed by $2Cl_3 \rightarrow 3Cl_2$, where M is a molecule of chlorine or of a foreign gas present in the system.[155] The collision cross-section for the recombination with emission of light (*i.e.* without involving a third molecule) has been estimated at $5{\cdot}4 \times 10^{-24}$ sq. cm. when the atoms are produced by irradiation of chlorine with light of wave-length 340 mμ. but only $0{\cdot}3 \times 10^{-24}$ sq. cm. when the wave-length is 411 mμ. and the atoms are separated with a much smaller kinetic energy.[156] It has been claimed that an emission of bluish light due to recombination of the atoms formed in chlorine heated at about 1000°C. can actually be observed.[157] From consideration of the energy surfaces of the chlorine atom and molecule, it has been calculated that the rate constants for the recombination of chlorine atoms in presence of helium, argon, hydrogen, nitrogen, and oxygen should be respectively 1·9, 2·5, 2·2, 2·8, and $2{\cdot}7 \times 10^{-32}$ (mole/c.c.)$^{-2}$ sec.$^{-1}$ (temperature not stated).[158]

The high-temperature equilibrium between chlorine atoms and molecules is considered under physical properties (see page 535) and the part played by chlorine atoms in thermal and photochemical reactions of chlorine with hydrogen, carbon monoxide, etc. is dealt with elsewhere (see pages 373 and 392)

Formation of Triatomic Chlorine.

Quantum-mechanical calculations have indicated that in the equilibrium $Cl + Cl_2 \rightleftharpoons Cl_3$, the formation of Cl_3 molecules should be favoured; the activation energy for the forward reaction is probably about 4·5 kg.-cal./mole, and for the reverse reaction 8·6 kg.-cal./mole ($\Delta H = -4{\cdot}1$ kg.-cal./mole for Cl_3 formation).[159] As noted above, the conception of Cl_3 molecules has proved useful in explaining the kinetics of recombination of chlorine atoms produced by photodissociation, and several authors have concluded that Cl_3 molecules play a part in the hydrogen–chlorine photochemical reaction. Apparently they react less readily with hydrogen molecules than do chlorine atoms. The collision efficiency for the reaction $Cl + Cl_2 \rightarrow Cl_3$ has been estimated to be $1{\cdot}78 \times 10^{-4}$. The reaction $2Cl_3 \rightarrow 3Cl_2$ occurs at every collision.[12,160-162]

Reactivity of Ionized Chlorine.

Ions produced in a stream of chlorine gas at atmospheric pressure by means of a point discharge are capable of initiating a chain reaction of chlorine with hydrogen. The effectiveness of either a positive or a negative ion in starting a reaction chain is of the same order as, and possibly rather greater than, that of a light quantum.[163]

From studies of the chlorine/chloride-ion exchange reaction and of the rate of chlorination of acetanilide,[164] it has been estimated that the velocity constant of the forward reaction in the equilibrium $Cl_2 + Cl^- \rightleftharpoons Cl_3^-$ in aqueous solution is at least 4×10^5 l. mole^{-1} min.$^{-1}$, and that of the reverse reaction at least 4×10^7 min.$^{-1}$, at 17°. Other information on the trichloride ion is given in the sub-section on chlorine solutions (see page 367). Free-energy and entropy data for aqueous chlorine ions are given in the sub-section on electrical properties (see page 347).

Photochemical Reactions Sensitized by Chlorine.

Chlorine molecules are dissociated into atoms by the absorption of blue or near-ultra-violet light, as already explained, and the atoms so formed are sometimes able to initiate chain reactions between two other substances, the consumption of chlorine in the reactions being frequently small or negligible. As examples may be cited the chlorine-sensitized combination of carbon monoxide and oxygen, the sensitized explosion of hydrogen with oxygen, and the sensitized oxidation of various carbon compounds, e.g. trichloroethylene.[165-167] This property of chlorine enables the reactions to be induced by light of a spectral region more readily accessible than that which could activate the other substances concerned.

Electron Emission during Reactions with Chlorine.

Electrons are emitted during the reaction of sodium-potassium alloy with chlorine at 10^{-6} to 10^{-3} mm. pressure. Energy-distribution and current-time curves have been determined.[168,169] Chlorine at low pressures also increases the emission of electrons by glowing platinum, provided that the temperature is below 1200°.[170]

CORROSION OF METALS BY CHLORINE

Some account of the general reactivity of chlorine towards metals has already been given. The following paragraphs refer to investigations of the attack of chlorine on metals, considered rather as a technological problem.

A detailed study of the high-temperature corrosion of 18 different metals has been made in the laboratories of E.I. du Pont de Nemours and Co., Inc.

TABLE XXVIII. - CORROSION OF METALS BY DRY CHLORINE

Metal	Approximate temperatures at which the given corrosion rate is exceeded in short-period tests (°C.)			Suggested maximum temperatures for continuous service (°C.)	
	0·0025 in./month	0·01 in./month	0·1 in./month	Brown et al. (du Pont)[110]	Friend and Knapp[171]
Nickel	510	590	680	540	540
Inconel	510	570	680	540	540
Hastelloy B	510	590	-	540	540
Hastelloy C	480	570	-	510	510
Hastelloy A	480	590	680	480	540
Chromel A	430	540	570	450	-
Magnesium	450	510	-	450	-
Monel	400	480	540	430	450
Stainless steel (18-8-Mo)	320	400	480	340	340
Stainless steel (18-8)	290	340	450	320	320
Platinum	480	540	570	260	>540
Hastelloy D	200	290	-	200	-
Copper (deoxidized)	180	260	290*	200	<260
Carbon steel	120	200	230†	200	<200‡
Cast iron	90	180	230†	180	200
2S Aluminium	120	150	180▲	120	-
Gold	120	180	200	-	-
Silver	40	120	260	-	?430

* Ignites at 320°C. † Ignites at 230 - 260° ▲Ignites at 200 - 230°

‡ Iron pipe has been known to inflame at about 200°C. (400°F.) in chlorine

Table XXVIII gives a selection of the values found for the rates of corrosion by dry chlorine, which was passed over the metal test-pieces for periods of 2 - 20 min. at a speed of (usually) 1·3 ft./min. The temperatures are quoted in °C., rounded off to the nearest 10°, though in the original report they are given to the nearest 50°F. The corrosion rates were calculated as inches of penetration per month, a procedure useful for comparison but unsound in view of the brevity of the test periods and the known fact that the progress of corrosion with time may follow a parabolic or other non-linear law. The fifth column of the table gives the maximum temperatures suggested for continuous industrial use of each metal, and the last column gives for comparison similar figures suggested by earlier workers (these also are rounded off to the nearest

10°C. after conversion from °F.).

The du Pont workers found that variation of the gas flow-rate over a wide range did not cause a variation in corrosion rate. The corrosion rates were roughly proportional to the vapour pressures of the chlorides involved. Moist chlorine (0·4% H_2O) caused increased attack even above the dew-point, but not above 370°C.; e.g. stainless steel showed a penetration by moist chlorine of 0·2 in. per month at 15°, 0·1 in. per month at 49°, 0·03 in. per month at 200° and 0·015 in. per month at 370°, but at higher temperatures the rate was as for the dry gas. The moist gas caused pitting of the specimens only at low temperatures.

With some metals, e.g. nickel, Inconel, and stainless steel in dry chlorine, the graph of the logarithm of the corrosion rate against temperature is a straight line. With platinum, however, the rate rises to a sharp maximum at about 580°C., falls to a minimum at about 660°, then rises again steadily; there is indication of another maximum at 370°. Gold shows a maximum rate at 270° (not very sharp), a minimum at 470° and thereafter a steady rise.[110] These effects are presumably connected with the volatility and stability at various temperatures of the metal chlorides.

Table XXIX gives figures which show how the average rate of attack by chlorine on mild-steel sheet (0·08–0·15%C) can vary with temperature and the length of the test period. The corrosion rate figures were calculated both as mg. of weight lost per square dm. per day and as inches of penetration per year.

TABLE XXIX.- CORROSION OF MILD-STEEL SHEET BY CHLORINE

Temp.	Corrosion loss over test periods of 30 min.		Corrosion loss over test periods of 8 hours	
°C.	mg./dm²./day	in./yr.	mg./dm²./day	in./yr.
77	41	0·007	34	0·006
107	78	0·014	-	-
135	130	0·023	-	-
166	220	0·040	53	0·010
198	310	0·057	59	0·011
230	445	0·080	54	0·010
240	500	0·083	60	0·011
247	535	0·096	57	0·010
251-2	$17{\cdot}5 \times 10^4$	31·54	-	-

The sudden increase in corrosion rate at 251° is ascribed to volatilization of ferric chloride, the effect of which as a protective coating is thus nullified. At intermediate temperatures, the formation of chloride causes a lower average corrosion rate over an 8-hour period than over a 30-minute period. The absence of such a diminution in the average rate at 77° is ascribed to inadequacy of the quantity or quality of the chloride coating formed during 8 hours.[109]

Iron is rapidly corroded by moist chlorine gas, or by chlorine water, at room temperature: both chlorine and hypochlorous acid are concerned in the process. Even traces of residual chlorine in chlorine-treated sea water lead to increased corrosion of steel pipe, especially at water velocities of 4ft. per sec. or higher.[172-174] Various ferrosilicon alloys have a much better resistance to moist chlorine than ordinary mild steel.[172,175,176]

Aluminium is stated to be resistant to dry chlorine at 20°C. but to be rapidly attacked at 250°. It is also rapidly attacked by the moist gas or the aqueous solution at 20°. Other metals having a poor resistance to moist chlorine are nickel and various nickel-rich alloys, brass and various bronzes, gold, platinum, and zinc.[172,177,178] With zinc, however, it is reported that corrosion by water containing up to 5 p.p.m. of chlorine is less than by distilled water.[179]

Lead is recommended for operations with dry chlorine at moderate temperatures, and can be used even with the moist gas up to 110°C. Tin is attacked by dry chlorine even at 20°.[172]

Tantalum has excellent resistance to wet or dry chlorine up to 150°C., but is severely attacked at 300°.[172,177] Titanium is reported to have outstanding resistance to chlorine saturated with water vapor, but not to the dry gas.[183]

A study[184] of the corrosion of sheet silver by chlorine, saturated with water vapor, gave the figures quoted in Table XXX.

TABLE XXX. - CORROSION OF SHEET SILVER BY CHLORINE

Temp. °C.	Gain in weight by AgCl formation			
	Average up to 20 hr.		Rate after 250 hr. exposure	
	mg./dm.^{2}/day	in./yr.	mg./dm.^{2}/day	in./yr.
10	67·3	0·0070	1·5 at	0·00015 at
25	75·5	0·0079	5·4 (170 hr.)	0·0008 (170 hr.)
44	123	0·0120	6·8	0·0007
64	50·9	0·0053	22·5	0·0023
90	32·6	0·0035	20·5	0·0021

The rate of reaction followed a parabolic law after 120 hr. (cf. page 381). Up to 280 hr. the most rapid corrosion was at 64°, but in a longer test the rate at 90° might prove higher. The corrosion process is considered to depend on diffusion of an aqueous solution of chlorine through the silver chloride film, and the apparent negative temperature coefficient may be explained by supposing that a tough film is more rapidly formed at higher temperatures.[134] Another worker considers that the rate of attack (presumably by dry chlorine) depends on the diffusion of silver ions into the chloride film, and claims that this diffusivity and hence the corrosion rate may be reduced by alloying a few per cent. of cadmium, zinc or lead with the silver. The same investigator also maintains that the thick silver chloride films are much less protective than thin ones.[96]

For data, mainly qualitative, concerning the resistance of numerous other metals and alloys to chlorine, the reader is referred to the tables given by Ritter[172] and by the editors of 'Chemical Engineering'[177] as well as to several articles in the latter journal.[185,186] This information is accompanied by data on the rate of attack by chlorine on various non-metallic materials of construction.

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THE PHOTOCHEMICAL REACTION OF CHLORINE WITH HYDROGEN

The photochemical combination of chlorine and hydrogen was intensively studied during the period 1920 – 1940, mainly with the object of elucidating the complicated kinetics of this stoicheiometrically simple reaction. With the full realization of the influence of traces of certain foreign substances on the reaction rate and with developments in experimental technique, most of the confusion which formerly prevailed has now been cleared away. This is due largely to the work of the research groups associated with the names of Bodenstein, Chapman, Allmand, Norrish and Rollefson. Their results also made an important contribution towards an understanding of the nature of chain reactions in general.

The following account summarizes first the experimental evidence and then the conclusions which have been drawn therefrom concerning the reaction mechanism.

Effect of the Wave-length and Intensity of the Light Irradiating the System.

The combination of hydrogen and chlorine may be brought about readily by absorption of light of any wave-length within the region (<478 mμ) where chlorine shows continuous absorption, and also in the region of weak banded absorption at least as far as 546 mμ.[1,2] A report of reaction at still higher wave-lengths, 730 mμ or more,[3] lacks confirmation. Evidence suggesting that, with very dry gases, a wave-length below 254 mμ is needed is no longer accepted. Determination of the relative quantum yields at various wave-lengths[2] gave values 0·10, 0·49, 0·53, 1·00, 0·67 and 0·22 respectively for the wave-lengths 260, 313, 365, 405, 436 and 546 mμ. Later work in the same laboratory[4] showed constant quantum efficiency between 490 and 400 mμ, 10–20% diminution between 400 and 290 mμ, and a gradual diminution above 490 mμ. A third paper[1] showed a diminution of yield in the ultra-violet region only when the total pressure was low (2 mm. Hg). The apparent rapid diminution of quantum yield above 490 mμ disappears if it is postulated that the reaction in this region is associated only with the continuum underlying the chlorine absorption bands.[5] On the whole it seems that the wave-length of the light is important only in so far as it determines the intensity and localization of the light absorption within the vessel.

There is agreement that, under ordinary conditions, the reaction rate is proportional to the first power of the absorbed light intensity.[6,7,8b] With mixtures of hydrogen and chlorine extremely carefully freed from oxygen and other inhibitors, however, several groups of workers have found that the rate varies with a fractional power of the absorbed intensity, e.g. with the 0·6 power,[9] or the 0·5 power,[10] or with a power varying between 0·05 and 1·0 according to conditions.[11a] The Bodenstein school always maintained that the first-power law holds under all conditions, but the most recent experiments by other workers confirm the approximation to a square-root law provided that the chlorine pressure is not too low.[12,13]

Variation of the Reaction Rate with the Hydrogen and Chlorine Concentrations. Wall Effects.

Several workers have found that, in the absence of oxygen, the reaction is of the first order with respect to the hydrogen pressure, but independent of the chlorine pressure except in so far as the latter affects the light absorption;[14,15] this is true provided that the chlorine pressure is not too low.[12,16] Older work, which appeared to show a variation of the reaction velocity with the square of the chlorine pressure, and virtual independence of the hydrogen pressure,[17-19] was probably vitiated by the presence of inhibitors. At high light-intensities and chlorine pressures, but with a low hydrogen pressure, a variation of reaction rate with the inverse square of the chlorine pressure has been observed.[11b]

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With oxygen present, the variation of reaction rate with the reactant concentrations becomes more complicated (see below).

It has been found that the reaction rate diminishes with falling total gas pressure (p). In capillary tubes the rate varied as $p^{2\cdot 5}$, whereas in wider tubes the effect of pressure disappeared above 30 mm. though the rate varied as p^3 in the pressure range 0·2 – 0·8 mm.[20b,21,22] Another report gives an increase in quantum yield from 20 to over 25,000 as the pressure increases from 0·01 to 60 mm.[23b] Workers of the Allmand school found, however, that the reaction proceeded 'normally' with chlorine pressures down to 0·012 mm. and hydrogen pressures at least down to 0·04 mm.[1,11a,24,25]

It has been shown that the reaction can be brought about by irradiation of a hydrogen-chlorine stream kept out of contact with any solid surface,[26] and hence that contact with such a surface is not necessary for initiation of the reaction (compare the thermal reaction, see page 373). Where, however, the reaction mixture is in contact with a containing vessel, the walls have a notable influence on the reaction rate, as may be inferred from the above-mentioned pressure effects and also from reports that the reaction proceeds less rapidly in narrow than in wide tubes, especially at low pressures.[20a,27] The quantum yields obtained vary considerably with the pre-treatment of the vessel and with the nature of the gas film adsorbed on it,[8b,12] and wall effects have been held responsible for the discrepancies between the results of various workers.[15] It has been supposed that, with inhibitor-free gas mixtures, the reaction rate may be limited solely by the removal of chlorine atoms at the wall of the vessel, possibly with the formation of a volatile compound of chlorine and silicon,[8b,14,28] but this is disputed (see page 394). In a silver vessel having a glass window protected from contact with the reacting gases, the characteristics of the reaction were similar to those observed in a glass vessel, but the quantum yields were very high:[29] it could be inferred that the rate of disappearance of chlorine atoms striking a chlorinated silver surface was only 1 per 10,000 impacts.[8b]

Temperature Coefficient of the Reaction.

The temperature coefficient, in white light, has been reported as 1·35 (for a 10° rise) between 30° and 73°C., diminishing to 1·16 between 135° and 177°.[14] Earlier workers found that this coefficient, in the range 0 – 40°, had a maximum value at 20° and increased as the light was changed from violet to blue-green;[30] this was later correlated with the temperature coefficients of light absorption by chlorine.[31] Workers of the Allmand school found that the temperature coefficient of the reaction increased gradually with wave-length over the range 310 – 436 mμ, even after allowing for change of absorption with temperature.[6b] They further found a rise (in the range 17 – 27°) from 1·34 at 436 mμ to 1·67 at 546 mμ; this indicated an apparent extra 4 – 5 kg.-cal./mole heat of activation at 546 mμ which was attributed to the need, at the latter wave-length, for the absorbing chlorine molecule to be in a higher vibrational level of the ground state if dissociation is to be brought about.[1] This explanation, however, encounters the difficulty that the proportion of molecules in the higher vibrational levels is too small at ordinary temperatures, and later measurements of the extinction coefficient at various temperatures have indicated that the high temperature coefficient of the reaction at 546 mμ may after all be sufficiently accounted for by the rapid variation of the absorption with temperature at that wave-length.[5,32]

It has been reported that the temperature coefficient of the reaction increases with the light intensity,[13] and with increasing purity of the reactants.[33,34]

Quantum Yields.

The quantum yields in the reaction naturally vary with the physical conditions and the freedom of the system from inhibitors and retarders. With oxygen-free gases various workers[2,9] have obtained about 10^5 molecules of hydrogen chloride per light quantum absorbed. An even higher yield, $4{\cdot}2 \times 10^6$, was obtained in a case where a special technique prevented any contact between glass and the reacting gases.[29] Those workers who have found a variation of the reaction rate with a fractional power n of the absorbed light intensity find, naturally, that the quantum yield varies inversely as $I_{\text{abs}}^{(1-n)}$.

With gases containing oxygen, the quantum yield of hydrogen chloride is still considerable. For example, with a mixture containing chlorine and hydrogen each at 42 mm., hydrogen chloride at 16 mm. and oxygen at 50 mm., from 117 to 120 molecules of hydrogen chloride per quantum were obtained at various light intensities.[7]

Effect of Water Vapour.

Several earlier workers reported that the hydrogen–chlorine photochemical reaction would not proceed in the absence of at least traces of moisture, unless short-wave ultra-violet light ($\lambda < 254$ mμ) was used.[35-39] These results were widely accepted for a time, and various theories were devised to account for the supposed participation of water molecules in the initiation of the reaction chains.[16,40-44] Later workers obtained evidence that the presence of water is not necessary for the reaction to occur in visible and long-wave ultra-violet light.[22,25,28,45] As a result of experiments showing that equal quantum yields are obtained with moist and with intensively dried gases,[46] it has been accepted that the earlier work was probably vitiated by the unwitting introduction of inhibitors and that water plays no important part in the reaction.

Effect of Oxygen and Other Inhibitors.

It has long been known that oxygen has a retarding effect on the reaction (Mellor, II, 151), and a number of workers have found that the reaction rate is inversely proportional to the oxygen pressure, except when this is very low.[7,8b,19,45,47-49] The quantum yield of hydrogen chloride remains considerable, as already noted, but water is simultaneously produced, and it is reported[50] that as the ratio of oxygen to chlorine increases the molecular ratio of the products water and hydrogen chloride approaches a limit between 1 and 2. The kinetics of this water formation are very complex.[49,51-53]

Photosensitized explosions of hydrogen–oxygen mixtures, due to absorption of light by admixed chlorine, can be brought about between 25° and 340°C.: in these reactions, water is formed exclusively if the pressure of the chlorine exceeds a certain limiting value, while with less chlorine hydrogen chloride is formed without explosion.[54-56]

It has been reported that hydrogen peroxide, as well as water, is formed in appreciable amount during irradiation of hydrogen–chlorine–oxygen mixtures,[57] although elsewhere it is said that chlorine atoms rapidly decompose hydrogen peroxide.[8b]

The hydrogen chloride produced in the hydrogen–chlorine photochemical reaction has itself a retarding effect on the reaction rate,[7,9,12] but this is probably slight unless oxygen is present in the system.[8,28]

The well-marked effect of ammonia, in causing an induction period before the reaction sets in (Mellor, II, 150 – 1), has been shown to be due to the time required for completion of a chlorine-sensitized photo-decomposition of the nitrogen trichloride which is formed initially from the ammonia and must be removed before the main reaction can proceed.[58,59]

Mechanism of the Reaction.

The chain character of the hydrogen–chlorine photochemical reaction was evident as soon as the high quantum yield was discovered (Mellor, II, 153). The nature of the links in the chain was long in dispute, but as early as 1918 Nernst[60] proposed a scheme which in essentials is now generally accepted (see next page).

(1) $Cl_2 + h\nu \longrightarrow 2Cl$	(initiation of chains)
(2) $Cl + H_2 \longrightarrow HCl + H$	(propagation of chains by successive reactions of atoms with H_2 and Cl_2)
(3) $H + Cl_2 \longrightarrow HCl + Cl$	
(4*a*) $H + H \longrightarrow H_2$	(termination of chains: only 4*b* is now considered important)
(4*b*) $Cl + Cl \longrightarrow Cl_2$	
(4*c*) $H + Cl \longrightarrow HCl$	

As described in the section on the chlorine spectrum (see page 627), it is now known that absorption by the chlorine molecule of light of any wave-length corresponding to the continuum extending below 478 mμ involves immediate dissociation of the molecule into atoms. (The atoms are either both in the ground state, $^2P_{3/2}$, or one is in the ground state and the other, in the state $^2P_{1/2}$, has[5] a small excitation energy, 0·1 e.V.). Hence it is now considered certain that the initiation step in the hydrogen-chlorine reaction, when brought about by light of wave-lengths corresponding to the continuum, is dissociation of the chlorine molecule, as postulated by Nernst, and earlier theories postulating initiation by excited chlorine molecules[23c] are regarded as untenable. There is also a strong probability that initiation is by dissociation even with light corresponding to the banded spectrum, since the latter has an underlying continuum, but here the possibility of initiation by excited chlorine molecules cannot be entirely excluded.[1,5]

That initiation normally occurs by dissociation of the chlorine molecule was confirmed by experiments showing that hydrogen chloride is formed when chlorine is irradiated and passed into a hydrogen atmosphere 10^{-4} sec. after the irradiation.[61] Under such conditions, excited chlorine atoms would have lost their energy and become inactive.

It has been said that only the $^2P_{1/2}$ chlorine atoms are capable of initiating the reaction chain,[16,62] but analysis of the chlorine spectrum indicates that $^2P_{1/2}$ atoms are produced only by light quanta corresponding to the long-wave end of the continuum, whereas the photochemical reaction is initiated by quanta corresponding to any part of the continuum.[32]

Evidence that the propagation steps involve hydrogen atoms was obtained by measuring their effect on the para-ortho hydrogen conversion.[8b,63] The reaction $H + Cl_2 \longrightarrow HCl + Cl$ is exothermic ($\Delta H^\circ = -45{\cdot}1$ kg.-cal./mole), but the reaction $Cl + H_2 \longrightarrow HCl + H$ is slightly endothermic ($\Delta H^\circ = 1{\cdot}0$ kg.-cal./mole)[64] and has a heat of activation which has been given as[45] 5·5 or[65] 6·1 kg.-cal./mole and is the main cause of the temperature coefficient of the over-all reaction. Hence[45,65,66] the reaction $H + Cl_2 \rightarrow HCl + Cl$ is very rapid, but the reaction $Cl + H_2 \longrightarrow HCl + H$ occurs with a collision frequency only of the order of 10^{-5}. The inhibiting effect of HCl, so far as it is real in oxygen-free gases (cf. above), lies in the reversal of the latter reaction.

The termination of the reaction chains in oxygen-free gases was supposed by the Bodenstein school, who always found a direct proportionality between reaction rate and light absorbed, to be brought about mainly by a first-order reaction involving chlorine atoms at the vessel wall.[8b,14] As has long been realized,[79,80] termination by bimolecular reactions between active centres, such as $Cl + Cl \longrightarrow Cl_2$ in the original Nernst scheme, necessarily involves variation of the reaction rate with the square root of absorbed light intensity; those workers who have found such a variation, or an approximation thereto (see page 391), have concluded that (at least at higher chlorine pressures and in vessels with a small surface/volume ratio) chain termination occurs mainly by recombination of chlorine atoms: $2Cl + M \longrightarrow Cl_2 + M$, where M is any molecule in the gas capable of taking up part of the recombination energy of the chlorine atoms.[9,66] A variation of this mechanism is the intermediate formation[12] of Cl_3 molecules: $Cl + Cl_2 + M \rightleftharpoons Cl_3 + M$, $2Cl_3 \longrightarrow 3Cl_2$ (cf. page 384).

In systems containing oxygen (where the linear light-intensity relation certainly holds) the main terminating reaction is probably $H + O_2 + M \rightarrow HO_2 + M$,[8b,50] followed by reactions giving ultimately water with perhaps a transient formation of hydrogen peroxide or chlorine dioxide. A reaction $H + HCl + O_2 \rightarrow H_2O + ClO$ has also been suggested.[7]

As an example of an attempt to fit in all the experimental facts, the kinetic scheme given in Bodenstein's last paper on the subject may be cited:[8b]

$$
\begin{array}{lll}
(1) & Cl_2 + h\nu = 2Cl & \propto I_{abs} \\
(2) & Cl + H_2 = HCl + H & k_2 \\
(3) & H + Cl_2 = HCl + Cl & k_3 \\
(4) & H + O_2 + M = HO_2 + M & k_4 \\
(5) & Cl + O_2 + HCl = HO_2 + Cl_2 & k_5 \\
(6) & Cl \text{ (on wall)} = \tfrac{1}{2}Cl_2 \text{ (or a} & k_6 \\
 & \quad \text{silicon-chlorine compound)} &
\end{array}
$$

The symbols on the right are the velocity constants of the various partial reactions. The HO_2 formed in (4) and (5) was supposed to react to give H_2O_2 or with Cl_2 to give ClO_2, these two products being rapidly decomposed by Cl and H atoms respectively. By the usual assumption of a steady concentration of chain-carriers, the kinetic equation derived was:

$$\frac{d[HCl]}{dt} = \frac{2k_3 I_{abs}[Cl_2]}{k_4[O_2][M] + \dfrac{k_3 k_5}{k_2}\dfrac{[O_2][HCl][Cl_2]}{[H_2]} \quad \dfrac{k_3 k_6}{k_2}\dfrac{[Cl_2]}{[H_2]}}$$

Here [M] is the sum of terms representing the effects of H_2, O_2, Cl_2, N_2, etc. and especially HCl molecules in assisting reaction (4), and also the wall effect on that reaction. This equation was shown to fit Bodenstein's experimental data reasonably well, though there was a tendency for the ratio $k_3 I_{abs}/k_4$ to diminish during the course of a run.

The second term in the denominator, representing inhibition by reaction (5), was held to be normally of secondary importance. The questionable feature of the equation is the third term in the denominator, which expressed Bodenstein's belief that in oxygen-free gases the chain-termination is entirely by reaction (6) (cf. above).

Other detailed reaction mechanisms are discussed in many papers,[7,12,18] and in various reviews of the reaction kinetics.[67-70]

Miscellaneous Evidence on the Hydrogen-chlorine Photochemical Reaction.

The expansion accompanying the onset of photochemical reaction in hydrogen-chlorine mixtures (Draper effect) has been studied by observing the refraction effects following momentary irradiation by a spark discharge ('schlieren' technique). It was found that with reactive mixtures, presumably free from oxygen, there was a delay of 0·01 sec. before any change was apparent. With less reactive mixtures, the maximum effect was attained sooner than with those which were more reactive; this corresponded with the shorter length of the reaction chains.[71]

By following the temperature changes after cutting off the light beam, the life-period of the reaction chains was found to be 0·025 - 0·05 sec. under particular conditions.[66,72] In a silver-lined vessel, with no contact between the gases and glass, a life-period estimated as 16 sec. was observed.[29]

Iodine is a catalyst for the reaction,[30,63,67] although in certain conditions a rate inversely proportional to $[ICl]^{1/2}$ was found.[62]

In addition to the photosensitized explosions of hydrogen and oxygen, mentioned earlier, mixtures of hydrogen and chlorine alone can be exploded by absorption of light (Mellor, II, 148). For such explosions, the relation between the critical ignition pressure (P) and the quantity of light energy absorbed (I) has been given as $\log (P/I) = (A/I) + B$, where A and B are constants.[73] Hydrogen-chlorine mixtures were found to be exploded by the light of burning magnesium provided that the hydrogen content was between 9·8 and 52%[74] (cf. page 374). In the light of a carbon arc, with mixtures containing 31·5, 40, 50, 60 and 76% chlorine, the lower explosion-pressure limits were found to be respectively 330, 60, 50, 30 and 350 mm.; oxygen had no effect on these limits if its concentration was less than 10%, but it raised the limits markedly at concentrations above 10%. Inert gases had effects related to their collision frequencies.[75]

The rate of photochlorination of deuterium at 0° and 32°C. has been determined as $\frac{1}{13}$ and $\frac{1}{10}$ respectively of the rate with hydrogen under comparable conditions.[76] However, another measurement of the rate ratio gave the value $\frac{1}{3}$, which was claimed to fit in with the difference between the zero-point energies of H_2 and D_2 molecules.[77]

Experiments on the reaction of hydrogen with chlorine, induced by the action of atomic hydrogen,[23a] α-particles,[78] *X*-rays,[81] or electrons,[82] have afforded confirmatory evidence that in the photochemical reaction the light plays no part other than the initiation of the reaction chains, which have similar properties with each mode of excitation.

It has been asserted that, during the photochemical formation of hydrogen chloride, rays with mitogenetic properties are emitted (the so-called Gurvich rays).[83]

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USES OF CHLORINE

General Statistics.

The manner in which chlorine is consumed in the United States, the largest producing country, has been classified by MacMullin as follows:

Estimated end-uses of chlorine made

	In 1940 %	Estimated usage, end of 1947 %	tons*
Pulp bleaching	21	11	175,000
Disinfectants and sanitation	6	4	63,000
Textiles	5	3	47,000
Chlorinated products	60	77	1,210,000
Miscellaneous	8	5	77,000
	100	100	1,570,000

* Presumably short tons, though this is not stated.

This author emphasizes that the rapid growth in chlorine usage since about 1933 is to be correlated with the growth of the organic chemical industry, especially the production of compounds derived from petroleum. About 70% of the chlorine made in the U.S.A. in 1947 was used in situ for the production of other chemicals, the consumption in manufacturing various organic chemicals (as estimated[1] at the end of that year) being shown in Table XXXI.

TABLE XXXI. - CHLORINE CONSUMPTION IN ORGANIC CHEMICALS

Product	Chlorine used tons/yr.	Product	Chlorine used tons/yr.
Monochlorobenzene (net)	120,000	Acrylonitrile	5,000
Dichlorobenzenes	35,000	Di(chloroethyl) ether	6,000
Phenol	64,000	Glycols and ethylene oxide	134,000
Diphenyl and diphenyl ether	5,000	Vinyl and vinylidene chlorides	62,000
Aniline	12,000	Neoprene*	21,000
Benzene hexachloride	3,000	Chloral	50,000
Bromine for ethylene dibromide	12,000	Amyl chlorides (net)	9,000
Carbon tetrachloride	150,000	Keryl chlorides	25,000
Chloroform	18,000	Chlorinated paraffin	10,000
Ethyl chloride*	50,000	Aluminium chloride (for alkylation)	40,000
Tri- and tetra-chloroethylenes	220,000	Others	109,000
Ethylene dichloride	50,000		

* The hydrogen chloride used was made partly from sodium chloride and sulphuric acid.

Another analysis of American chlorine usage, relating to the year 1948, is shown diagrammatically in Fig. 7. This differs in detail from the preceding, but exhibits similar features (again it is uncertain whether the long or short ton is the unit).[2]

The trends in the various uses of chlorine by American industry over the years 1945 - 1951 are further illustrated[3] in Fig. 8.

Comparable figures for other countries do not appear to be available.

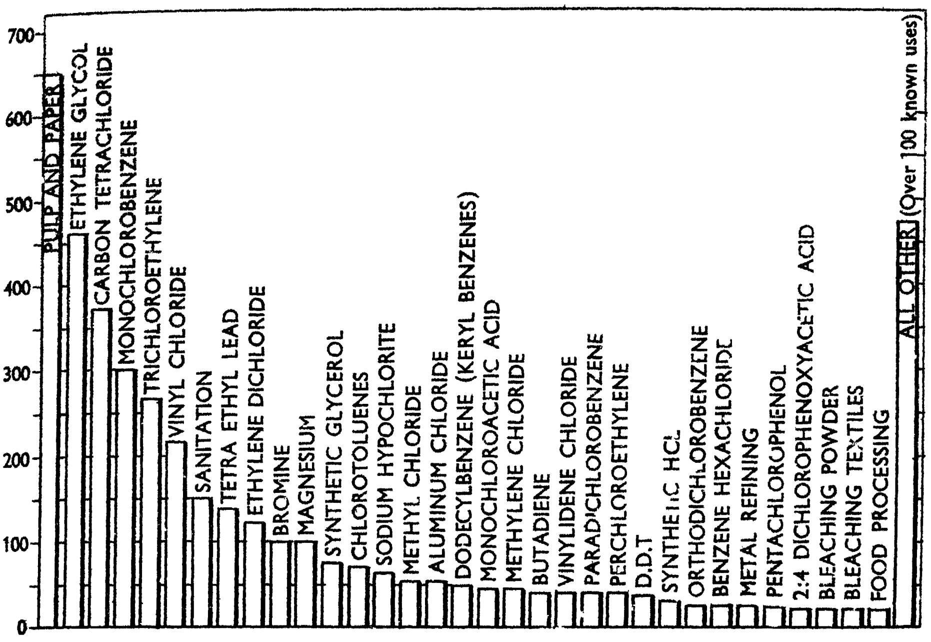

Fig. 7. USAGE OF CHLORINE IN U.S.A.

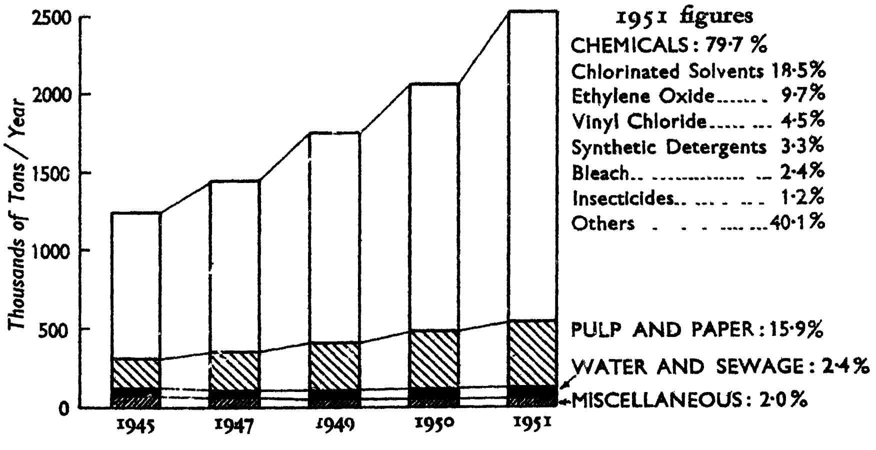

Fig. 8. CHLORINE CONSUMPTION BY AMERICAN INDUSTRY

Particular Uses.

The treatment of wood pulp in the production of paper and rayon forms what is probably the largest outlet for chlorine outside the chemical industry. This use depends on the fact that treatment of the pulp with chlorine in acid solution converts lignin, and other undesirable constituents, by means of substitutive reactions into substances soluble in water or alkali. Further treatment with chlorine in alkaline solution bleaches residual lignin and other colouring matter by oxidation [4-6]

The disinfectant properties of chlorine and hypochlorites have long been known (Mellor, II, 96), but the use of chlorine for sterilizing water supplies has expanded in recent years with the development of 'break-point' chlorination. This process consists in adding chlorine to the water until the apparent chlorine content, after rising to a maximum and falling to a low minimum (the break-point), suddenly begins to rise again steadily in proportion to the further chlorine added. The apparent maximum and minimum in the chlorine content are very probably due to the formation and subsequent decomposition of chloramines formed by reaction of chlorine with ammonia or certain types of organic amino-compounds present in the water before treatment (e.g. $2NH_3 + Cl_2 \rightarrow 2NH_2Cl + 2HCl$; $2NH_2Cl + Cl_2 \rightarrow N_2 + 4HCl$). Prior to the break-point the chlorine exists in combination with nitrogen, but afterwards it is in the free state and the water is found to be more reliably sterilized than if insufficient chlorine had been added to reach the break-point. Other advantages claimed for the process are that the taste, odour and colour of the water are improved, that pipe-lines are kept clear of growths which would reduce their carrying capacity, and that dissolved manganese is removed.[7-12] A review of the subject has been given by Palin.[13]

Chlorine has also been used to reduce the biochemical oxygen demand of sewage by a break-point process.[14] Break-point phenomena with sewage can be very complex owing to the presence of several chlorine-demanding substances.[15]

The sterilizing action of chlorine has been held to be due to inhibition of glucose oxidation at the appropriate point in the bacterial cell.[16] Hypochlorous acid, formed by hydrolysis of the chlorine, is apparently the effective agent. The effect of concentration (c) and killing time (t) required with *B. anthracis* spores can be expressed by the equation $K = c^n t$. The difference in the resistance of various types of organism and (in part) the lesser efficiency of mono- and di-chloramine may be connected with the differing rates of diffusion through the cell walls.[17] The bactericidal action of chlorine is less rapid than that of ozone, and more care is required to avoid after-tastes.[18,19]

Among the other uses of chlorine which depend on its toxicity are its employment for sterilizing the process liquors in sugar manufacture,[20-22] the control of mussels etc. in sea-water cooling circuits,[23] and the restoration of the output of wells (here the chlorine may also help by removing calcium and magnesium deposits).[24-26]

Chlorine is used extensively in the textile industry, not only for the preparation of bleach liquors (calcium hypochlorite, etc.), but also to reduce the shrinking propensity of woollen fabrics.[27,28] The latter effect is due to rupture by chlorine of the disulphide linkages in the fibre.[29,30] Chlorinated wool is dyed more readily than untreated wool.[31,32] It has also been proposed to use chlorine to impart a curl to jute fibres.[33]

Chlorine is used in various ways in metal refining, e.g. to remove occluded gases from aluminium and its alloys,[34-36] to remove hydrogen from magnesium,[37] and for 'parting' gold or removing zinc from lead.[38] It can also be used to strip tin from scrap tin-plate[39] and to modify the conductivity of selenium.[40,41]

Miscellaneous actual or proposed uses of chlorine are for removing

Refs. p. 401

hydrogen sulphide from waste gases,[42] or mercury vapour from air, or sulphur from metallurgical coke,[43] or mineral impurities from graphite;[44] as a catalyst in hydrocarbon cracking;[45] for the decomposition of phosphate rock[46] or the working-up of manganese ore;[47] and for 'killing' cyanides in industrial waste waters by oxidizing the cyanides to cyanates.[48-50]

Other examples of the industrial use of chlorine will be found on pages 689 and 815, and in subsequent Supplements. For details of the use of chlorine in the production of organic compounds, the reader is referred to works on organic chemical technology.

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SECTION XIV

THE PREPARATION AND MANUFACTURE OF HYDROGEN CHLORIDE AND HYDROCHLORIC ACID.

By C. C. ADDISON and J. LEWIS

DIRECT UNION OF THE ELEMENTS

The burning of chlorine in hydrogen is one of the most important methods for the manufacture of hydrochloric acid. The gases are prepared by the electrolysis of brine, and are not normally given drying treatment before reaction. Small quantities of air may be introduced with the chlorine into the combustion chamber to lower the combustion temperature.[1] To ensure the formation of chlorine-free hydrogen chloride, an excess (up to about 15%) of hydrogen is employed. If air is introduced also, a chlorine-free product is obtained provided that the hydrogen present is sufficient to react with both the chlorine and the oxygen.[2,3] The reaction has been carried out over a wide range of gas pressures, from values exceeding 1 atm.[4,5] to pressures as low as 5 – 20 mm. of water.[6] The reaction is initiated by igniting the hydrogen in a stream of air by means of a coal gas flame; chlorine is then introduced into the combustion chamber, and the air supply reduced or stopped when steady burning has commenced. Under these conditions conversion of chlorine into hydrogen chloride is complete, although the burning of hydrogen and chlorine in the presence of catalysts such as finely divided activable clay[7] or quartz[8] has been suggested. Combustion may take place in large vertical towers or in a multiplicity of small globes; if the burners and reaction vessels are of metal, corrosion by the wet gases is minimised by incorporating jackets of cooling water which maintain the temperature of the metal above the dew point of hydrogen chloride. The relation between dew point and moisture content of hydrogen chloride is given below:[8,9]

H_2O content (vol-%)	0·5	1·0	2·0	3·0	4·0	5·0	6·0	10·0
Dew point °C.	28	37	47	53	57	60	63	71

In practice the moisture content may vary over the above range, but is typically between 1 and 3%. If a liquid film saturated with metal chloride were allowed to form on the metal surface, its vapour pressure would be lower than that of the uncontaminated condensate, and the film would dry more slowly. To avoid this difficulty, the extent to which the temperature of the cooling jacket exceeds the dew point varies with the deliquescent nature of the metal chloride; thus with iron vessels the optimum cooling jacket temperature is 15° above the dew point, whereas with copper vessels an excess of 3° is adequate. An alternative method of protecting the burners is to supply the gases under pressure, so that the velocity of the gas stream is greater than the rate of flame propagation.[10,11,12] This prevents contact between the flame and the burners, but the critical gas velocity necessary to give a steady flame is difficult to maintain. A form of burner in industrial use overcomes corrosion difficulties by the use of silica as fabricating material throughout. The burner consists of two vertical concentric tubes;

hydrogen is supplied through the outer tube (2 – 3 in. diameter) and chlorine through the inner tube (1 in. diameter). The latter terminates several inches below the outer tube, and carries a series of fishtail fins designed to ensure uniform mixing of the gases. The burner is surmounted by a cylindrical silica combustion tower approx. 5 ft. high and 1·5 ft. diameter.

The hydrogen chloride gas is cooled by passage through water-cooled ceramic tubes, and absorbed in towers packed with silica chips through which a counter-current of water is flowing. Rates of flow may be adjusted to give hydrochloric acid (laboratory 'concentrated') of sp. gr. 1·18 (11·3N.). Other methods involving direct absorption of the hot gaseous product are possible. For example, combustion can be carried out in an open mouthed chamber submerged in a quantity of the acid; the flame impinges directly on the liquid which is circulated and maintained at a temperature a few degrees below the b.p. of the acid.[13] Alternatively, the gases may be burned under high pressure at silica burners immersed in water.[14]

Chlorine and hydrogen combine under the influence of light; the kinetics of this classical example of a photochemical reaction are considered in detail under the properties of chlorine. The rate of combination at room temperature is represented by the equation $\frac{d[HCl]}{dt} = kI[H_2]$ (where I is the intensity of the absorbed light), at low temperatures (down to 200°K.) by the equation:-

$$\frac{d[HCl]}{dt} = \frac{kI[H_2]}{1 + k'[HCl][Cl_2]} \quad (\text{where } k' \leqslant 0{\cdot}1),$$

and at temperatures below the m.p. of chlorine by the equation $\frac{d[HCl]}{dt} = kI^{1/2}[H_2]$.[15,16] The reaction was found to be inhibited by nitrogenous impurities;[17] this is due to the formation of nitrogen trichloride.[18] The postulate that water vapour must be present for reaction to occur[19] has been shown to be incorrect.[16,20,21] The high quantum efficiency of hydrogen chloride formation is reduced by addition of carbon dioxide, nitrogen, argon, neon or helium.[22] The presence of oxygen not only contributes to the induction period, but also has a marked effect on the rate of reaction. The rate in the presence of oxygen is given by the expression:-

$$\frac{d[HCl]}{dt} = \frac{kI[H_2][Cl_2]}{m[Cl_2] + [O_2]([H_2] + [Cl_2]/10)};$$

for oxygen pressures greater than 0·04 mm. the term $m[Cl_2]$ may be eliminated.[15] Hydrogen and chlorine combine thermally at temperatures above 200° The thermal reaction is more complicated than the photochemical reaction, since thermal combination is initiated by dissociation of chlorine molecules on the surface of the containing vessel, whereas photochemical combination is initiated in the gaseous phase.[23] At 200° the chain length for the thermal reaction is about 10^4, compared with 10^6 for the photochemical reaction.

ACTION OF CHLORINE ON HYDROGEN COMPOUNDS

Chlorine reacts with water to produce hydrochloric and hypochlorous acids. At 25° water dissolves about twice its volume of chlorine; the solution evolves oxygen on standing (or more rapidly in sunlight) owing to the decomposition of hypochlorous acid leaving a pure aqueous solution of hydrochloric acid. Hydrogen chloride is produced directly from chlorine and water by heating chlorine with an excess of water vapour at 1000 – 1600° in the absence of reducing agents:[24] ($2Cl_2 + 2H_2O = 4HCl + O_2$). A high yield of hydrogen chloride has been obtained at 900° in the presence of a catalyst consisting of a mixture of magnesium chloride with magnesium and calcium oxides.[25] Reaction occurs between chlorine and water in the liquid phase in the presence of carbon to produce hydrogen chloride and carbon dioxide, the speed of reaction depending upon the temperature, the chlorine concentration and the activity of the carbon.[26,27] When steam and chlorine are passed through a bed of hot carbon the reaction is exothermic and may be controlled (at about 600°) so that it proceeds according to the equation:-

$$2Cl_2 + C + 2H_2O = CO_2 + 4HCl$$

The presence of combustible constituents (hydrogen and carbon monoxide) in the gaseous product, formed by the reaction $C + H_2O = CO + H_2$ (or the reaction below), may be avoided by the use of steam and chlorine in equimolecular quantities and by close control of the quantity of carbon employed.[28,29,30] The experimental conditions may readily be modified to produce a mixture of hydrogen chloride with carbon monoxide, by the reaction $Cl_2 + C + H_2O = CO + 2HCl$.[31] The process is used to recover small quantities of chlorine from gaseous mixtures. For example, the chlorine may be adsorbed by coke or charcoal from dilute gaseous mixtures; when steam is passed through the carbon layer at 250–800° hydrogen chloride is produced.[32] When a non-reactive gas such as nitrogen or methane, containing 1–4% of chlorine, and a similar quantity of air is mixed with water vapour in amount at least equivalent to the chlorine content of the gas and passed through carbon the chlorine is converted into hydrogen chloride in the temperature range 100 – 400°.[33]

Hydrogen chloride and carbon are produced when hydrocarbons (*e.g.* turpentine) react with chlorine, and the direct chlorination of brown coal has been proposed as a method of hydrogen chloride manufacture.[34] With gaseous hydrocarbons the reaction may be carried out suitably by burning a mixture of the hydrocarbon (or a hydrocarbon-containing gas such as coal gas) and chlorine in a flame in an atmosphere of air. A burner of the bunsen type may be used[35,36] Alternatively, the gases may be mixed to form an inflammable or explosive mixture at a temperature below the ignition temperature, and the combustion then effected in a controlled manner.[37] When chlorine and simple hydrocarbons are heated separately to a temperature between 600° and 1000°, and then brought together, the gases react spontaneously to give hydrogen chloride and carbon.[38] The same products are obtained by burning a partially chlorinated hydrocarbon with a hydrocarbon, chlorine, or another chlorinated hydrocarbon, provided that the total number of gram-atoms of chlorine does not exceed that of hydrogen. The use of mixtures containing methyl chloride (or carbon tetrachloride) with methane and chlorine has been described.[39] Hydrogen chloride is also readily separated from the products of the partial chlorination of hydrocarbons. In the partial chlorination of methane the chlorinated hydrocarbons boiling below 15° may be separated, together with hydrogen chloride, from the higher-boiling chlorinated hydrocarbons by scrubbing the gas mixture with a carbon tetrachloride-chloroform mixture. Hydrogen chloride is then separated from the gaseous mixture by washing with water.[40] The preparation of hydrogen chloride free from carbon and organic impurities may be effected by adding water vapour to the chlorine-hydrocarbon mixture in an amount at least sufficient to convert the hydrocarbons into carbon monoxide.[41] When a compressed mixture of methane and chlorine, with excess of water vapour, is passed through a tube at 700 – 800°, the formation of chlorinated organic compounds is avoided, and the chlorine is converted quantitatively to hydrogen chloride. The reactions are:-

$$CH_4 + 3Cl_2 + H_2O = CO + 6HCl$$

$$CH_4 + 4Cl_2 + 2H_2O = CO_2 + 8HCl$$

By operating at the lower temperature and increasing the excess of water vapour the second reaction is promoted.[42]

The reaction $2Cl_2 + 2H_2O \longrightarrow 4HCl + O_2$ (the reverse of the Deacon process for the manufacture of chlorine) takes place readily in the presence of reducing agents capable of removing the oxygen produced; these reactions employ carbon for this purpose, but sulphur dioxide is a suitable alternative. The reaction $SO_2 + Cl_2 + 2H_2O = H_2SO_4 + 2HCl$ goes to completion in the temperature range 15 – 90°, the reaction rate increasing with rise of temperature.[43] Reaction may be carried out by bubbling the dry gases into water (or hydrochloric acid solution), or by mixing the gases, saturated with water vapour, in a suitably designed nozzle discharging into a cooling coil, from which the products may be transferred to a distillation chamber.[44] The hydrochloric acid may be removed from the sulphuric–hydrochloric acid mixture by heating to above 100° [45] The reaction proceeds in the presence of air and the extent of reaction is independent of the quantity of air present.[46] Some excess of sulphur dioxide over the amount required according to the above equation is also converted into sulphuric acid in the presence of air; on this reaction chlorine has a catalytic effect reminiscent of the behaviour of nitrogen oxides in the lead chamber process for manufacturing sulphuric acid. It is stated[43] that the reaction $SO_2 + Cl_2 + H_2O = SO_3 + 2HCl$ does not take place.

Although water and hydrocarbons represent the main sources of hydrogen in these reactions, ammonia and hydrogen sulphide have also been proposed for this purpose. At low temperatures, reactions between chlorine and ammonia are unsuitable because of the formation of ammonium chloride: $3Cl_2 + 8NH_3 = 6NH_4Cl + N_2$, and nitrogen trichloride: $3Cl_2 + NH_3 = NCl_3 + 3HCl$. However, when anhydrous ammonia and anhydrous chlorine are brought into contact in a reaction chamber containing calcium chloride and at a temperature of 800°, the products are hydrogen chloride and free nitrogen: $3Cl_2 + 2NH_3 = 6HCl + N_2$.[47] The reaction between chlorine and hydrogen sulphide: $Cl_2 + H_2S = 2HCl + S$ is facilitated by mixing equimolecular proportions of the two gases in the presence of sulphur mono- or di-chloride.[48] The latter serves as a sulphur solvent which is not influenced by the reactants, and may be removed from the hydrogen chloride by washing the gaseous product with xylene.

THE ACTION OF HYDROGEN OR HYDROCARBONS ON CHLORINE COMPOUNDS

Under suitable conditions hydrogen or the simple hydrocarbons will react with many chlorine compounds. With metal chlorides the products are hydrogen chloride and free metal or the metal hydride. Even the alkali metal chlorides may be reduced in this way. At temperatures above 700° hydrogen reacts with sodium chloride to produce hydrogen chloride and sodium hydride.[49, 50] With methane the yields are lower than with hydrogen. Silica and iron oxide are often added to the metal chloride to reduce the endothermic nature of the reaction; the reaction between methane and sodium chloride may be represented thus:-[50,51]

$$4NaCl + 8SiO_2 + 3Fe_2O_3 + CH_4 = 2Na_2SiO_3 + 6FeSiO_3 + CO + 4HCl.$$

Lithium and potassium chlorides undergo reduction by hydrogen or methane at 800 – 1000°, and the yield of hydrogen chloride obtained at a given temperature decreases with increase in the heat of formation of the chloride.[52] For the reduction of magnesium chloride the temperature should be above 700°, and above 900° for reducing the chlorides of calcium, strontium and barium.[49, 53] In the presence of silica and iron oxide, the formation of hydrogen chloride from calcium chloride by the action of hydrogen is quantitative at 1000°, and 75% at 700°. When methane is used instead of hydrogen, the yields are somewhat lower.[54] With anhydrous zinc chloride, the maximum yield of hydrogen chloride (about 50%) from reaction with hydrogen is reached at 500 – 550°. By the use of methane, the yield is reduced to about 27%.[55] Silver chloride is reduced quantitatively by hydrogen at 540°, and by methane or butane at about 750°

Lead chloride is reduced by methane above 800°, and cuprous chloride by methane above 600°. Reactions involving the metals silver, lead or copper have been suggested as a means of recovering hydrogen chloride from waste gases; the gases are passed over the metal to form the chloride, and the hydrogen chloride regenerated in an anhydrous state by reaction of the chloride with hydrogen or hydrocarbons.[56]

With volatile chlorides, reduction may be carried out in the gaseous phase. Reduction of mercuric chloride vapour by hydrogen or hydrocarbons takes place at 600°; the mercury may be condensed from the gas stream, and (when hydrocarbons are used for reduction) the finely divided carbon may be separated by a dust precipitator.[56] Similarly, aluminium chloride may be reduced by hydrogen by passing the vapour in a stream of hydrogen through an electric arc.[57] A vapour-phase reaction involving boron trichloride is used in the preparation of hydrogen chloride and pure amorphous boron.[58] Boron trichloride is prepared by the action of chlorine on borax in the presence of powdered charcoal:

$$Na_2B_4O_7 + 7Cl_2 + 7C = 4BCl_3 + 7CO + 2NaCl$$

The boron trichloride is condensed from the gas stream from the furnace, re-vaporised, and reduced by passage of the vapour with hydrogen through an electric furnace; boron dust is suspended in the furnace atmosphere to catalyse the reaction $2BCl_3 + 3H_2 = 6HCl + 2B$. In another method a mixture of nitric oxide and hydrogen chloride (from which the latter may readily be obtained by scrubbing with water) is formed by the reaction $2NOCl + H_2 = 2HCl + 2NO$. Nitrosyl chloride and hydrogen are heated together in the temperature range 150 – 500°; a temperature of 400° has been found suitable in the presence of catalysts such as Al_2O_3, MnO_2, $MnCl_2$, Cr_2O_3, SiO_2 or activated charcoal, or when the mixture is irradiated by light.[59, 60, 61]

THE DECOMPOSITION OF CHLORIDES BY LESS VOLATILE ACIDS

This is the method commonly employed for the preparation of hydrogen chloride gas in the laboratory. The method described in Mellor (II,162), involving reaction between concentrated sulphuric acid and solid sodium chloride in a Kipp's apparatus, suffers from several disadvantages, including the necessity to dismantle the apparatus for recharging, and to use separate drying equipment. These difficulties are partly overcome by dropping a saturated solution of sodium chloride into sulphuric acid,[62] but hydrogen chloride is most conveniently prepared by direct reaction of concentrated hydrochloric with sulphuric acid[63-66] or chlorosulphonic acid.[67] A convenient apparatus for this purpose is shown in Figure 1.[66] Dropping funnels *G* and G_1 contain equal volumes of concentrated hydrochloric acid (sp. gr. 1·17) and sulphuric acid. The acids are allowed to drip from the funnels (the latter acid at about twice the rate of the former) and to mix in the annular space *B*. The hydrogen chloride evolved passes up arm *A*. The concentrated sulphuric acid flows over loosely-packed glass wool or short lengths of glass tubing in arm *A*, and therefore serves as a drying column for the issuing hydrogen chloride.

Although much hydrogen chloride is now manufactured by the processes already described above the salt cake (sulphuric acid–salt) process, and Hargreaves' process (in which a mixture of sulphur dioxide, air and steam is passed over salt at about 530°) are still of importance, and a large number of references in the patent literature (not considered here) relate to improvements in the efficiency of these two processes by modifications in temperature, relative quantities of reactants and design of reaction chambers. Similar processes may be carried out using potassium chloride[68, 69] and calcium chloride[70, 71] in place of sodium chloride. Several important modifications of these processes, in which other acids replace sulphuric acid, have been found

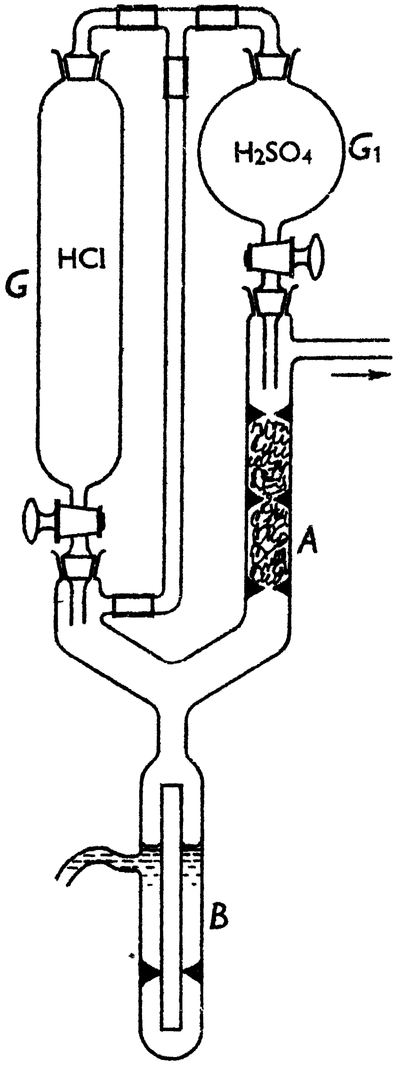

Fig. 1. APPARATUS FOR THE PREPARATION OF HYDROGEN CHLORIDE

practicable. Reaction occurs between salt, sand and steam at elevated temperatures to give sodium silicate and hydrogen chloride: $2NaCl + H_2O + SiO_2 = Na_2SiO_3 + 2HCl - 68$ kg.-cal. Reaction begins at about 600°, increases gradually up to 1000°, and becomes markedly greater at slightly above 1000°.[72] Low yields of hydrogen chloride at higher temperatures are attributable to the unfavourable equilibrium constant for this reaction; writing $K = (HCl)^2/(NaCl)^2 (H_2O)$, then $\log_{10} K = 2{\cdot}9$ at 1000°K., 1·2 at 1200°K., and 0·1 at 1400°K.[73-75] The addition of air to the steam increases the decomposition of the salt, but the process is then complicated by the reactions:-

$$4NaCl + 2SiO_2 + O_2 = 2Na_2SiO_3 + 2Cl_2$$
$$\text{and } 4HCl + O_2 = 2H_2O + 2Cl_2.$$

Hydrogen chloride may be also produced by heating together ortho-, pyro- or meta-phosphoric acid with alkali metal chlorides, the residues being utilised as fertilisers.[76,77] Nitric acid may be used in a similar way, but the volatility of nitric acid is a disadvantage.[78,79] The distillate from a chloride-nitric acid mixture contains both hydrochloric and nitric acids; the acids may be separated by adding the distillate slowly to concentrated sulphuric acid, when hydrogen chloride is immediately liberated.[80] The gaseous product obtained on heating an alkali metal chloride with excess of concentrated nitric acid contains substantial quantities of nitrosyl chloride, which may be scrubbed from the gas mixture by the use of water sufficiently hot to prevent excessive dissolution of hydrogen chloride.[81] Treatment of an alkali metal chloride with hydrofluoric acid, or a complex acid of the type H_2SiF_6 or HBF_4, has also been suggested for the preparation of hydrogen chloride, although in such reactions the preparation of pure fluorides is usually of primary importance.[82-85]

THE HYDROLYSIS OF CHLORIDES

When chlorides are hydrolysed using controlled amounts of water ($MCl + H_2O = MOH + HCl$) hydrogen chloride is readily separated because of its volatility. Some non-metal chlorides are hydrolysed immediately on contact with water. For example, when water is added to an excess of phosphorus trichloride, hydrogen chloride is continuously evolved and the reaction: $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$ proceeds to completion. Certain oxy-compounds may also be employed for this purpose; thus the hydrolysis of sulphuryl chloride has been proposed as an industrial process.[86-89] Many other non-metal chlorides (*e.g.* silicon tetrachloride) react similarly. The chlorides of a number of metals in their highest valency state hydrolyse on contact with water; stannic chloride is hydrolysed by moist air, and the reaction $TiCl_4 + 2H_2O = TiO_2 + 4HCl$, which readily occurs when titanium tetrachloride is ejected from a spray nozzle into moist air, has been utilised for the production of naval smoke screens. These reactions may be adapted for the continuous production of hydrogen chloride by mixing the vapour of the chloride with controlled amounts of water vapour.[90]

The chlorides of the most electropositive metals may also be hydrolysed at sufficiently high temperatures. Hydrolysis of magnesium, calcium and sodium chlorides in a current of steam has been utilised industrially. The chemistry of these processes has already been described (Mellor,II,164) and more recent modifications have been concerned primarily with preliminary treatment of the halides, or the addition of catalysts, to promote reaction or give a higher yield of hydrogen chloride.[91-100] The equilibrium constants and free energies of the reactions:-

$$CaCl_2 + H_2O \rightleftharpoons CaO + 2HCl$$

$$\text{and}\quad CaCl_2 + SiO_2 + H_2O \rightleftharpoons CaSiO_3 + 2HCl$$

have been compared. The difference between the ΔH values for the two reactions is about 28 kg.-cal. for temperatures between 30 and 600°. The amount of hydrogen chloride liberated increases with rise of temperature, especially in the second reaction. Yields greater than 90% may be obtained from the second reaction at 400°.[101] Hydrolysis of chlorides by deuterium oxide has proved a convenient method for the laboratory preparation of deuterium chloride, this compound has been prepared, for example, by passing deuterium oxide over magnesium chloride at 600°.[102] Hydrolysis of ferric chloride may be accomplished at 300 – 600°, without the addition of steam, by simply heating the the hydrated salt. If hydrated ferrous chloride is used, it must be heated in the presence of air or oxygen.[103,104]

PURIFICATION OF HYDROGEN CHLORIDE AND HYDROCHLORIC ACID

Most methods of preparation involve the initial production of hydrogen chloride gas, and many of the possible impurities may be removed conveniently by treatment at this stage. Sulphur dioxide is removed by scrubbing the hydrogen chloride with sulphuric acid. At concentrations in the range 80–100%, and at temperatures of 50–150°, sulphuric acid readily absorbs sulphur dioxide and moisture, but is a poor solvent for anhydrous hydrogen chloride.[105] Sulphur dioxide may also be removed by bringing the gas, in the presence of oxygen, into contact with an aqueous solution of calcium chloride containing hydrochloric acid in concentration equilibrium with the gas phase; calcium sulphate is precipitated from the solution.[106] Organic contaminants are removed from hydrogen chloride by the addition of oxygen and (if necessary) a combustible gas such as butane. Ignition of the mixture oxidises the hydrocarbons to carbon monoxide and dioxide, and the hydrogen chloride in the product may then be dissolved in water.[107,108] Arsenical contamination may be largely eliminated (down to 0·00004%) by bubbling hydrogen chloride through a solution of calcium hypophosphite;[109] at the same time chlorine and sulphur dioxide are also removed by the reactions:-

$$3H_3PO_2 + 4AsCl_3 + 6H_2O = 3H_3PO_4 + 12HCl + 4As$$

$$H_3PO_2 + 2Cl_2 + 2H_2O = H_3PO_4 + 4HCl$$

$$H_3PO_2 + SO_2 = H_3PO_4 + S$$

The method suffers from the disadvantage that the hypophosphorous acid undergoes some spontaneous decomposition: $2H_3PO_2 = H_3PO_4 + PH_3$. Part of the phosphine so produced passes on with the hydrogen chloride stream, and is trapped as phosphonium chloride in the final aqueous solution. However, when the gas stream is passed through a bed of activated carbon, arsenic chloride is preferentially adsorbed, and the final product shows no trace of arsenic by the Gutzeit or Marsh test.[110] Other suitable adsorbents are silica gel, activated bauxite or charcoal.[111-113] Hydrogen chloride gas is absorbed by several of the heavy metal sulphates (*e.g.* copper, cadmium, bismuth, lead, zinc, silver and mercuric sulphates), either in the solid form or in suspension in concentrated sulphuric acid. (The nature of these addition compounds is discussed under the chemical properties of hydrogen chloride, see page 462). This reaction is utilised in several processes for the removal of hydrogen chloride from gas streams; the gas is passed over the solid sulphate (copper sulphate being commonly employed) and the hydrogen chloride regenerated by heating the solid.[114-119] These compounds also provide a convenient means of storing and transporting anhydrous hydrogen chloride.[120] Purified hydrogen chloride may be dried by treatment with concentrated sulphuric acid; industrial processes employ counter-current flow in a tower.[121,122] Final traces of moisture are removed by passing the gas through a mass of granular aluminium chloride.[123,124] Anhydrous hydrogen chloride can be liquefied at 60 atm. pressure, and in this state it may be stored in steel vessels.[125,126]

Reagents employed for the purification of hydrochloric acid solutions have been discussed and summarised (Mellor II, 165). Further work has confirmed the use of stannous chloride (the Bettendorf reaction) in the removal of arsenic compounds.[127] In addition, arsenic, iron compounds and organic impurities are removed by passing the solution through a filter bed of activated charcoal.[128,129] Acid oxides of nitrogen are removed by treating the solution with sulphamic acid or its salts, followed by distillation.[130]

The choice of materials from which to fabricate vessels for the storage and transport of hydrochloric acid is limited by the highly corrosive nature of the solution. Use may be made of antimony or bismuth or their alloys,[131] or

Refs. p. 410

tantalum,[132] but the acid is usually stored and transported in vessels made from, or lined with, glass or ebonite.

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SECTION XV.

THE PHYSICAL AND CHEMICAL PROPERTIES OF HYDROGEN CHLORIDE AND HYDROCHLORIC ACID.

By C. C. ADDISON and J. LEWIS

THE PHYSICAL PROPERTIES OF HYDROGEN CHLORIDE

DENSITY

The density of solid hydrogen chloride undergoes a sharp change at the transition point (98·4°K.). The density of the rhombic modification, stable below the transition point, has been found experimentally to be 1·507 at 81°K.,[1] and 1·503 at 78°K.[2] Extrapolation of data in the latter experiment indicates a density of 1·54 at 0°K.[2] The density at 95°K., calculated from unit cell dimensions, is 1·55.[3] The experimental value for the density of the cubic modification, stable above 98·4°K., is 1·469 at 107°K.[1] Calculation from cell dimensions gives values of 1·48[3] and 1·49[4,5] for the density of the cubic form at the transition temperature.

Little information is available on the density of liquid hydrogen chloride beyond that already given (Mellor, II, 174); the variation in the density (d) of the liquid with temperature (T°K.) is expressed by the equation[6] $d = 1{\cdot}187 + 0{\cdot}00318\,(T_1 - T)$ where T_1 is the boiling point.

DEVIATION FROM IDEAL GAS BEHAVIOUR

These deviations have been most frequently expressed in terms of the constants a and b in Van der Waals' equation $(p + a/v^2)(v - b) = RT$. If v_1 is the ratio of the measured volume of one gram mol. of the gas to the volume of one gram mol. of the ideal gas at S.T.P., then the equation becomes

$$(p + a/v_1^2)(v_1 - b) = T/273{\cdot}1.$$

Using this equation for hydrogen chloride, $a = 731 \times 10^{-5}$ and $b = 1822 \times 10^{-6}$ when p is expressed in atmospheres.[7] Using the actual volume v_2 (mls.), the equation may be written

$$(p + a_1/v_2^2)(v_2 - b_1) = (1 + a_1)(1 - b_1)T/273{\cdot}1$$

when $a_1 = 3{\cdot}62 \times 10^6$ and $b_1 = 40{\cdot}2$.

Deviation from ideal behaviour has been expressed in terms of a compressibility coefficient λ, defined as

$$p_0 v_0 / p_1 v_1 = 1 + \lambda;$$

where v_1 is the volume of gas at atmospheric pressure p_1 and 0°, and v_0 the volume at an infinitely small pressure p_0. The average of 45 determinations on hydrogen chloride gave $1 + \lambda = 1{\cdot}00787$.[8] The deviation has also been expressed in the form $pv/RT = 1 + \beta/v$; β, the second virial coefficient, has the value -446 for hydrogen chloride.[9]

VISCOSITY

Values for the viscosity of gaseous hydrogen chloride (η dyne sec. cm.$^{-1}$)

are given in Table I.[10-13]

TABLE I. - VISCOSITY OF GASEOUS HYDROGEN CHLORIDE

T°C.	0°	21°	54°	99°	154°	200°	250°
$\eta \times 10^7$	1313	1434	1600	1832	2093	2303	2530

The mean free path l is related to the density ρ and mean molecular velocity $\bar{c}$ by $\eta = 0{\cdot}499\rho\bar{c}l$;[14] using $\eta \times 10^7 = 1397$ at 15°, then $l \times 10^6 = 4{\cdot}44$.[15]

The variation in gaseous viscosity with temperature is expressed with accuracy over a wide temperature range by the Sutherland formula[16]

$$\eta_1/\eta_2 = (T_1/T_2)^{½} \times [1 + (C/T_2)]/[1 + (C/T_1)].$$

Accurate determinations at $t_1 = 100{\cdot}3$°C. and $t_2 = 12{\cdot}5$°C. gave $\eta \times 10^7 = 1397 \pm 3$, and $1838 \pm 0{\cdot}4$ respectively, from which the Sutherland constant $C = 357$.[13] This equation may be written in the form

$$T = KT^{3/2}/\eta - C$$

which is convenient for graphical determination of C.[17] Using this equation, the values of the constants have been found to be $C = 359$, $K \times 10^6 = 18{\cdot}66$.[18]

The empirical equation $\eta = aT^n/(T + b)$ fits the viscosity data for hydrogen chloride over a wider range of temperature. For the range 23° to 750°, the values $a = 1{\cdot}9012 \times 10^{-5}$, $n = 3/2$, and $b = 387{\cdot}3$ give η values accurate to about 0·1%.[12] The simple relation $\eta = \eta_0(T/273{\cdot}1)^n$ gives satisfactory results for hydrogen chloride when the empirical constant $n = 1{\cdot}03$.[19]

GASEOUS DIFFUSION

The rate of diffusion of hydrogen chloride into itself, or into another gas of very similar molecular weight and diameter, has been determined from a study of mixtures of hydrogen chloride and deuterium chloride.[20] The coefficient of self-diffusion D (which is the quantity diffusing per second through 1 sq.cm. under a concentration gradient of unity) depends upon temperature and pressure; at 295°K., measurements on HCl-DCl mixtures containing from 63 to 71% HCl gave a mean value of D = 0·1246 cm.^{2}/sec. (corrected to 760 mm. pressure). This value is in fair agreement with coefficients of self-diffusion for other gases, e.g. 0·174 for carbon monoxide and 0·109 for carbon dioxide.[21]

THERMAL DIFFUSION

This property merits reference here, since hydrogen chloride was the first compound in which complete separation of the chlorine isotopes was achieved by the methods of thermal diffusion.[22] On the application of a temperature gradient to a gaseous binary mixture of molecules of different mass, the heavier molecules tend to diffuse towards the region of lower temperature, and the lighter molecules in the opposite direction, thus setting up a concentration gradient in each constituent. The process continues until balanced by gaseous diffusion; it is the more pronounced the greater is the mass difference between the two constituents but decreases rapidly with pressure;[23] the difference between the mol. fractions of either constituent at the high and low temperature regions is given by

$$\Delta\lambda = K_T \log_e (T_2/T_1)$$

Though the coefficient of thermal separation (K_T) is relatively small in isotopic mixtures, conditions in hydrogen chloride are favourable in that neither of the isotopic forms is present in small concentration, normal hydrogen chloride containing 75·7% $H^{35}Cl$ and 24·3% $H^{37}Cl$. The effects of thermal diffusion have been enhanced by enclosing the gas in a vertical tube, cooled on the outside and carrying down the centre an electrically heated wire.[24] Thermal diffusion sets up an isotope concentration gradient across the tube; convection currents then carry the heavier isotope to the bottom, and the lighter isotope to the top of the tube. The best separation has been obtained using five columns (each between 6 and 9 metres in length) connected in series; each column had an internal diameter 8·4 mm. and carried axially a 0·4 mm. platinum wire heated to about 700°.[25] After operation for 37 days, the chlorine from the hydrogen chloride withdrawn from the bottom of the column had an atomic weight of 36·956.[26] Assuming the atomic weight of ^{37}Cl to be 36·968, the hydrogen chloride gas contained 99·4% of $H^{37}Cl$. Hydrogen chloride withdrawn from the 'light' end of the apparatus contained 96% of $H^{35}Cl$ and further modification of the apparatus increased this to 99·6%. Hydrogen chloride containing 95% $H^{35}Cl$ has also been obtained using a single column 7·5 metres long.[27]

THE CRITICAL CONSTANTS

When liquid hydrogen chloride is heated in a confined space, its density ρ_L (g./ml.) varies with temperature (°K.) according to the equation[28]

$$\rho_L = 1{\cdot}706 - 0{\cdot}00276\, T$$

Values for the critical density ρ_c (g./ml.), the critical temperature t_c (°C.) and the critical pressure p_c (atm.), which in the case of t_c and p_c are in closer accord than the values previously quoted (Mellor,II,175), are given in Table II.

TABLE II. - CRITICAL CONSTANTS OF HYDROGEN CHLORIDE

ρ_c	t_c	p_c	Ref.
0·42	-	-	29
-	51·8	83·6	30
-	51·4	81·55	31
-	51·1	80·49	32
0·424	51·7	81·6	33

The critical temperature for many binary deuterium compounds is slightly lower than for the corresponding hydrogen compounds; t_c for deuterium chloride is 50·3°C.[34]

BOILING AND MELTING POINTS: HEATS OF FUSION AND VAPORIZATION

The m.p. of hydrogen chloride is given as 158·91°K.[35] and 159·34°K.[36] Of these two values, the former appears to be preferable. The b.p. is 188·07°K.[35] The m.p. of deuterium halides are a few tenths of a degree lower than those of the hydrogen halides; the m.p. of deuterium chloride is given as 158·44°K.,[37] and 158·2°K.[38]

From direct calorimetric measurement, the heat of fusion of hydrogen chloride is found to be 504·5 g.-cal. per mol.[36,39] and 476·0 g.-cal. per mol.[35] Corresponding calculations of the heat of fusion from measurements of the vapour pressure of solid and liquid hydrogen chloride gave values of 498·2 and 462 g.-cal. per mol. respectively, the difference arising from the different vapour pressure values assumed. The heat of fusion of deuterium chloride is 473·2 g.-cal. per mol.[37] On the assumption that the molal volumes for gas, liquid and solid are approximately the same for HCl and DCl, a value of 141 g.-cal. per mol. for the heat of fusion of deuterium chloride has been calculated.[38] This calculated value is not in accord with experimental evidence, which shows that (in common with the other hydrogen halides) the heat of fusion of deuterium chloride is only a few calories lower than that of hydrogen chloride.

The heat of vaporization has been found by calorimetric measurement to be 3860 ± 4 g.-cal. per mol.,[35] which is the mean of twelve concordant values: it is appreciably in excess of values already reported (Mellor,II,176). An indirect determination, assuming the gas to be perfect, gave 4040 g.-cal. per mol.[40]

VAPOUR PRESSURE

The vapour pressures of solid hydrogen chloride over a range of temperatures are given in Table III.[35]

TABLE III.- VAPOUR PRESSURE OF SOLID HYDROGEN CHLORIDE

T°K.	P (mm. Hg)
132·48	5·58
132·82	5·89
135·20	7·87
139·23	13·08
143·00	20·44
145·77	27·82
148·44	37·05
154·29	66·92
155·04	72·21
158·91 (triple point)	103·71

These values are related very closely by the equation

$$\log_{10}P(\text{mm. Hg}) = -\frac{1114}{T} - 1{\cdot}285\log_{10}T - 0{\cdot}0009467T + 12{\cdot}005$$

and also by the equation (due to Henglein[40]):-

$$\log_{10}P(\text{mm. Hg}) = -k/T^n + 7{\cdot}5030$$

where $k = 1966{\cdot}3$ and $n = 1{\cdot}1600$.

Independent determinations are in close agreement with the above values. Thus $P = 75{\cdot}6$ mm. at 155·55°K.,[41,42] and at 159·34°K. (quoted as the triple point), $P = 103{\cdot}44$ mm.[36]

The values of the vapour pressure of liquid hydrogen chloride[43] previously quoted (Mellor,II,176) appear to be somewhat low. More recent data, determined over the full temperature range for the liquid state, are given in Table IV.

These values are related by the equation[42]

$$\log_{10}P(\text{mm. Hg}) = -\frac{905{\cdot}53}{T} + 1{\cdot}75\log_{10}T - 0{\cdot}0050077T + 4{\cdot}65739$$

The equation of Henglein[40] has also been applied to the P-T relation for liquid hydrogen chloride, when $k = 945{\cdot}7$ and $n = 1{\cdot}0160$.

The vapour pressures of deuterium chloride, in both solid and liquid states, (see Table V), are slightly lower than the corresponding hydrogen chloride values.[38]

If P_1 and P_2 are the vapour pressures of hydrogen chloride and deuterium chloride respectively at the temperature T, then for the solid state

$$\log_{10}\frac{P_1}{P_2} = -\frac{57{\cdot}7}{T} + 0{\cdot}387$$

TABLE IV. - VAPOUR PRESSURE OF LIQUID HYDROGEN CHLORIDE

T°K.	P (mm. Hg)
158·91	103·71
164·62	162·9
169·28	229·8
173·95	317·1
178·53	428·1
181·84	526·4
185·17	643·4
188·41	774·8
191·96	943·9
195·93	1165·1

TABLE V. - VAPOUR PRESSURE OF DEUTERIUM CHLORIDE

T°K.	P (mm. Hg)	State
152·6	54·5	Solid
154·7	67·5	Solid
157·1	84·5	Solid
157·6	88·0	Solid
159·5	104·0	Liquid
168·2	205·5	Liquid
175·0	329·0	Liquid
181·0	486·5	Liquid
188·3	757·5	Liquid
195·9	1131·5	Liquid
200·9	1474·5	Liquid

and for the liquid state

$$\log_{10}\frac{P_1}{P_2} = \frac{15{\cdot}4}{T} - 0{\cdot}075$$

The ratio of the two vapour pressures reaches a maximum of 1·05 at the triple point.

SPECIFIC HEATS AND ENTROPY

Values for the molecular heat capacity C_p of solid and liquid hydrogen chloride are given in Table VI.[33]

TABLE VI. - MOLECULAR HEAT CAPACITY OF HYDROGEN CHLORIDE

Temp. °K.	C_p g.-cal./degree	Temp. °K.	C_p g.-cal./degree
SOLID		92·96	7·849
17·29	1·031	117·30	10·14
26·85	2·330	138·79	10·95
35·82	3·393	155·06	11·65
48·62	4·472	LIQUID	
58·94	5·231	163·72	13·89
72·63	6·159	171·45	13·95
80·25	6·712	178·64	14·01
87·70	7·327	185·20	14·07

The values of C_p for the solid show a discontinuity due to a solid transition which occurs at 98·36°K. (This transition is discussed under solid hydrogen chloride). These values were determined by direct calorimetric measurement; they are close to those determined by other workers using similar techniques[39,44] but are probably the most nearly correct.

Many determinations of the specific heat of gaseous hydrogen chloride have been made, both by direct measurement and by calculation from spectroscopic data. Table VII gives the values of the molecular heat at constant volume (C_v).[45]

TABLE VII. - MOLECULAR HEAT OF HYDROGEN CHLORIDE AT CONSTANT VOLUME

Temp. °K.	273	373	473	773	1473	2273
C_v g.-cal./degree	5·00	5·09	5·27	5·46	6·13	6·9

Values, calculated[46] from Raman spectra data,[47] for the molecular heat at constant pressure are given in Table VIII.

TABLE VIII. - MOLECULAR HEAT OF HYDROGEN CHLORIDE AT CONSTANT PRESSURE

Temp. °K.	300	600	800	1000	1200	1400	1600	1800	2000
C_p g.-cal./degree	6·95	7·07	7·28	7·54	7·78	7·98	8·14	8·28	8·38

The constants have been evaluated in the empirical specific heat equation, $C_p = a + bT + cT^2$, and are found to be 6·7319, $0{\cdot}4325 \times 10^{-3}$ and $3{\cdot}697 \times 10^{-7}$ respectively.[48] Ignoring cT^2, the values of a and b have been given as 6·70 and $0{\cdot}84 \times 10^{-3}$.[49] The specific heat of deuterium chloride is somewhat greater than that of hydrogen chloride at corresponding temperatures.[37]

The ratio of the specific heats at constant pressure and constant volume, $\gamma = C_p/C_v$, determined from the velocity of sound in the gas, is 1·404 at 0°C.[50] The entropy (S) of hydrogen chloride gas at the boiling point (188·07°K.) has been determined from calorimetric data by adding to the graphical integration of the equation $S = \int_0^T C_p d\ln T$ the entropy changes accompanying each change of state, as follows:

Entropy change	*g.-cal./degree per mole*
0°K. to transition point (98·36°K.)	7·36
Solid transition rhombic → cubic	2·89
Transition point to melting point (158·91°K.)	5·05
Fusion	3·00
Melting point to boiling point (188·07°K.)	2·36
Vaporization	20·52

This gives a total of 41·2 g.-cal./degree per mol.,[35] or 41·3 g.-cal./degree when corrected to the ideal state. At 298·1°K., entropy values of 44·5[35] and 45·4[39] g.-cal./degree have been determined. The former value is preferred, and is in close agreement with values obtained by calculation from spectroscopic data;[35,51] these calculations have been applied to $H^{35}Cl$ and $H^{37}Cl$ separately, giving the following values of S at 298·1°K; $H^{35}Cl$ = 44·619, $H^{37}Cl$ = 44·783, and the existing HCl mixture 44·658 g.-cal./degree.[52]

HEAT AND FREE ENERGY OF FORMATION

Direct calorimetric measurements of the syntheses $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) = HCl\ (g)$ have given the heat of formation of gaseous hydrogen chloride ($-\Delta H$

kg.-cal. per mol.) as 21·89 at 21°C.[53] and 24°C.[54] and 22·06 at 25°C.[55] The value of 21·89 kg.-cal. per mol. has also been calculated from measured values of ΔH for silver chloride, and the e.m.f. of the cell Ag|AgCl|HCl|aq. H_2.[56] The change in heat content for the above reaction, determined accurately from the e.m.f. of the hydrogen-chlorine cell, and spectroscopic data, gives $-\Delta H$ = 22·028 kg.-cal. per mol. at 25°C.[52] The heat of formation at 400°C., calculated using ΔH at 0°C. and specific heat data, is found to be 22·54 kg.-cal. per mol.[57] The free energy ΔG for this synthesis is given as a function of temperature over the range 298 – 2100°K. by the relation

$$\Delta G = A + BT \log T + CT$$

where $A = -21{\cdot}77$, $B = 9{\cdot}9 \times 10^{-4}$ and $C = -5{\cdot}22 \times 10^{-3}$.[58] Measurements of the free energy of formation at 298°K. give $\Delta G = -22{\cdot}775$,[55] and $-22{\cdot}741$ kg.-cal. per mol.[59]

As is to be expected from the large heat of formation, the hydrogen chloride molecule has a high thermal stability. Calculated values of the percentage dissociation into $H_2 + Cl_2$ are[60]

T°K.	500	1000	2000	3000
% dissociation	$1{\cdot}92 \times 10^{-8}$	$1{\cdot}34 \times 10^{-3}$	0·41	1·30

while ultraviolet radiation is said to cause about 0·25% dissociation.[61]

OPTICAL CONSTANTS, DIELECTRIC CONSTANT AND POLARIZATION

The refractive index n and the molar refractivity $R = (n^2-1)M/(n^2+2)\rho$ are compared in Table IX with corresponding values for deuterium chloride;[62] n_0 is the refractive index of the gas at 0°C. and 760 mm., referred to a vacuum.

TABLE IX. - MOLAR REFRACTIVITY OF HYDROGEN CHLORIDE AND DEUTERIUM CHLORIDE

Wave length λ (A.)	Hydrogen chloride		Deuterium chloride	
	$(n_0-1) \times 10^6$	R	$(n_0-1) \times 10^6$	R
6562·9	443·4	6·625	442·3	6·609
5893·0	445·6	6·658	444·5	6·642
5460·8	447·4	6·685	446·4	6·670
4916·0	450·2	6·727	449·4	6·715
4358·3	454·7	6·794	453·7	6·779

The mean value of $R_{HCl} - R_{DCl}$, 0·015, does not vary appreciably with wave-length. The value of n_0 decreases with increasing wave-length, and this effect continues into the infra-red.[63]

The earliest determination of the dielectric constant of gaseous hydrogen chloride gave $\epsilon = 1{\cdot}00258$ at 100°C. and 760 mm.[64] Later measurements of ϵ at atmospheric pressure, using a heterodyne beat null method in a temperature range of about 400° from just above the liquefaction point,[65] are given in Table X.

Independent measurements are in close agreement.[66] The values conform to the Debye equation, written as $(\epsilon-1)vT = AT + B$, where v is the specific volume and A and B are constants having the values 0·00104 and 0·895 respectively.

The variation with temperature of the total molar polarization, P, of hydrogen chloride is compared in Table XI with that of deuterium chloride (using as standard ϵ for air = 1·000582).[67]

Other P values determined over the temperature range 286 – 373°K. agree closely with those quoted in the Table.[68] The atomic polarization (P_a) of

TABLE X. - DIELECTRIC CONSTANT OF GASEOUS HYDROGEN CHLORIDE AT ATMOSPHERIC PRESSURE

T°K.	$(\epsilon - 1) \times 10^4$
201·4	74·52
260·1	47·16
294·2	37·92
359·2	26·72
433·9	19·48
503·9	15·26
588·8	11·82

TABLE XI. - VARIATION WITH TEMPERATURE OF THE TOTAL MOLAR POLARIZATION OF HYDROGEN AND DEUTERIUM CHLORIDES

T°K.	291·0	321·6	323·1	497·9	516·5
P_{HCl} c.c.	31·49	29·04	-	21·3	20·75
P_{DCl} c.c.	31·79	-	29·35	21·54	21·05

hydrogen chloride is very small; calculation from infra-red data gives P_a = 0·017 c.c.[69] Using the value 6·84 c.c. for the contribution of the atomic and electronic polarization ($P_A + E$), the above data give the dipole moment μ_{HCl} = 1·084 × 10^{-18} e.s.u., and μ_{DCl} = 1·088 × 10^{-18} e.s.u. The difference $\mu_{DCl} - \mu_{HCl}$ varies between 0·003 × 10^{-18} and 0·007 × 10^{-18}, according to the method of calculation.[67]

The above value for μ_{HCl} is believed to be the most reliable; other values (in Debye units) determined from dielectric constants are 1·034,[65] 1·18,[66] 1·48[70] and 1·06.[68] More widely divergent values have been obtained by the molecular beam method (1·95[71] and 0·91[72]) and by wave-mechanical calculation (1·23).[73] Polarization measurements on gaseous hydrogen chloride have also been applied to the study of the distance of separation of the nuclei under these conditions.[70]

The dipole moment of hydrogen chloride is generally higher when measured in solution in non-polar solvents than in the gaseous state. Values of μ measured in various solvents are collected in Table XII.

TABLE XII. - DIPOLE MOMENT OF HYDROGEN CHLORIDE IN VARIOUS SOLVENTS

Solvent	$\mu_{HCl} \times 10^{18}$	ϵ of solvent
Carbon tetrachloride	1·06[74]	2·22
Chloroform	1·04[77]	5·2
n-Heptane	1·19[74]	1·91
n-Hexane	1·03[77]	1·86
*cyclo*Hexane	1·26[78]	2·01
Benzene	1·25[74] 1·26[76] 1·21[77]	2·27
Toluene	1·24[77]	2·37
Ethyl bromide	1·02[75]	9·5
Ethylene dichloride	0·97[75]	10·58
1:4-Dioxan	2·12[74]	2·2
Diethyl ether	2·22[77]	4·68

It is clear from the Table that the μ values fall into two groups, and that the dielectric constant of the solvent is not a significant factor in determining the order of magnitude of the dipole moment; it is rather the case that high values of μ are associated with the presence of oxygen in the solvent. Spectroscopic[79] and potentiometric[80] evidence indicates the absence of appreciable ionization in HCl–dioxan solutions. The large solvent effect probably results from incipient hydronium formation; the H–Cl bond has its usual partial ionic character, but is in a slightly perturbed state because of the proximity of ether oxygen with its slightly negative charge, and these solutions show absorption bands in a region that can be ascribed to the perturbed hydrogen chloride molecule.[74] Similar considerations apply to solutions in diethyl ether; the value of μ_{HCl} in ether is nearly equal to the sum of the moments of the HCl and Et_2O molecules. The Raman spectrum of concentrated solutions of hydrogen chloride shows no strong HCl lines, which is in contrast with results for solutions in chloroform.[77]

Measurements of the dielectric constant of liquid hydrogen chloride are available only over a narrow temperature range near the freezing point. The values given in Table XIII were determined at a frequency of 3000 kilocycles.[81]

TABLE XIII. - DIELECTRIC CONSTANT OF LIQUID HYDROGEN CHLORIDE

T°K.	158·5	159·2	160·4	161·2	163·8	165·2
ϵ	10·643	10·583	10·536	10·488	10·298	10·202

The dielectric constant decreases regularly with rising temperature; extrapolation to 183°K. confirms an early single value, $\epsilon = 8{\cdot}85$, for that temperature quoted by Mellor (II, 180). The following values have been obtained at lower frequencies and 161°K.:[82]

Frequency (K_c)	60	20	0·3
ϵ	13·08	13·15	14·05

Although the absolute values for the dielectric constant of solids may be in some doubt owing to the possibility of spaces between crystals, they are of value in a relative sense; changes in the molecular rotation and dipole orientation at the solid transition point give rise to sharp changes in the dielectric constant of solid hydrogen chloride. The change in dielectric constant of the solid with temperature is shown in Fig. 1. The measured value of ϵ varies widely with the frequency, particularly above the transition temperature, but at any frequency there is a sharp isothermal change in dielectric constant at the transition temperature.

IONIZATION POTENTIAL

The ionization potential of hydrogen chloride gas has been given as 13·2V.,[83] 13·3V.,[84-86] 12·9V.[87] Experiments in which gaseous hydrogen chloride was ionized under impact of electrons from a heated tungsten filament have shown that this ionization potential is not a measure of the energy required to split the molecule into a hydrogen ion and a chloride ion; results show that electron impacts ionize the gas by the process $HCl \rightarrow (HCl)^+ + e$, and that the process $HCl \rightarrow H^+ + Cl^-$ does not occur.[84] Using the mass spectrograph, the following ions have been identified in the system: H^+, $(HCl)^+$, $(HCl)^{2+}$, Cl^+, Cl^{2+}, Cl^{3+}, Cl^{4+}, Cl^{5+} and Cl^-. Table XIV shows the minimum values of the energy required to produce some of these ions.[87]

In the presence of traces of moisture in the experimental tube, the ions H_2^+, Cl_2^+ and $(H_2O)^+$ were also observed; Cl_2^+ was observed only at high pressures and is thought to be a secondary product.

HYDROGEN CHLORIDE IN NON-AQUEOUS SOLVENTS

Table XV gives the solubilities of hydrogen chloride in some hydrocarbons

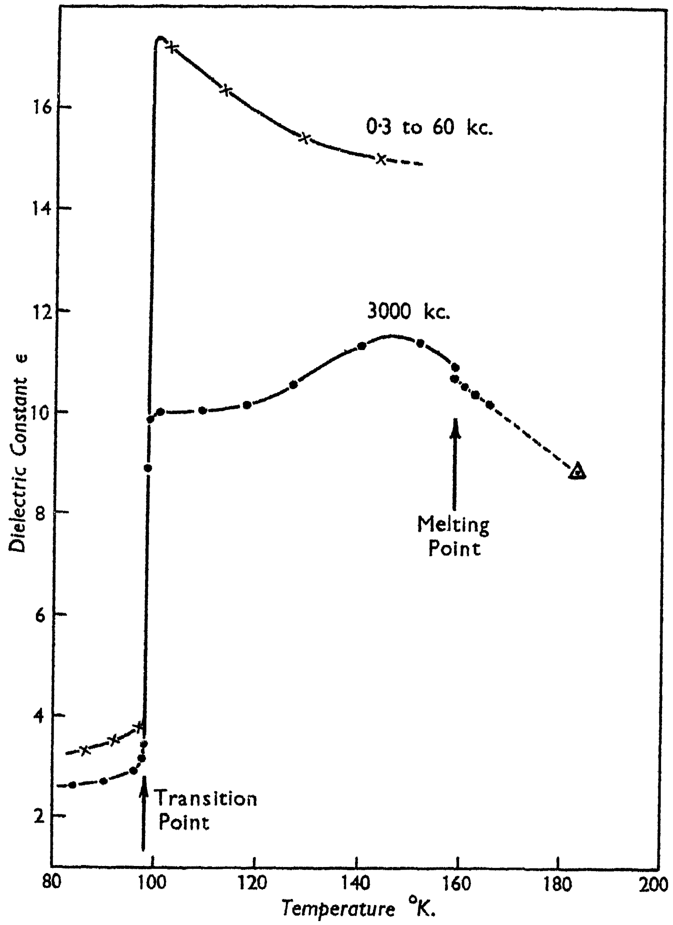

Fig. 1. RELATION BETWEEN TEMPERATURE AND DIELECTRIC CONSTANT OF SOLID HYDROGEN CHLORIDE

TABLE XIV. - MINIMUM VALUES OF ENERGY REQUIRED FOR IONIZATION

Ion	Appearance Potential (volts)	Probable process
H^+	18·6	$HCl \rightarrow H^+ + Cl$
$(HCl)^+$	12·9	$HCl \rightarrow (HCl)^+$
$(HCl)^{2+}$	35·7	$HCl \rightarrow (HCl)^{2+}$
Cl^+	17·2	$HCl \rightarrow H + Cl^+$
Cl^{2+}	45·7	-
Cl^{3+}	~160	-
Cl^-	~1·2	$HCl \rightarrow H + Cl^-$

and halogenated hydrocarbons. Two methods of analysis have been used:

(1) the dry gas was bubbled through the solvent until this was saturated; the hydrogen chloride was then displaced from solution by a stream of carbon dioxide-free air, and absorbed in water;[88] (2) hydrogen chloride was brought into contact with the solvent in a gas burette, and the solubility determined from the volume change.[89]

TABLE XV. - SOLUBILITY (N = MOL. FRACTION HCl AT 20° AND 760 MM.) OF HYDROGEN CHLORIDE IN HYDROCARBONS AND HALOGENATED HYDROCARBONS

Solvent	N	Solvent	N
Hexane	0·0197	Chloroform	0·0444
Octane	0·0296	Bromobenzene	0·0305
Dodecane	0·0314	Chlorobenzene	0·0315
Cetane	0·0270	Benzyl chloride	0·0448
*cyclo*Hexane	0·0154	Benzotrichloride	0·0275
Carbon tetrachloride	0·0181	*sym.*-Tetrabromoethane	0·0236
	0·0155	*sym.*-Tetrachloroethane	0·0265
Benzene	0·0425		0·0274
Toluene	0·0507	Ethyl bromide	0·1019
Tetrachloroethylene	0·0163	Ethylene dichloride	0·0457
Trichloroethylene	0·0206		0·0399
Pentachloroethane	0·0214	Ethylene dibromide	0·0344
	0·0225	Trichloroethane	0·0310
Bromoform	0·0306		
Ethyl bromide	0·0348		

The solubilities in oxygen-containing solvents are usually higher, and values for a range of such solvents are given in Table XVI.[90,91]

TABLE XVI. - SOLUBILITY (N = MOL. FRACTION HCl AT 1 ATM.) OF HYDROGEN CHLORIDE IN SOLVENTS CONTAINING OXYGEN

Solvent	t°C.	N	Solvent	t°C.	N
Anisole	20	0·100	Diphenyl ether	25	0·0494
	30	0·083		30	0·0442
	40	0·066	$\beta\beta'$-Dichloroethyl ether	20	0·149
Phenetole	10	0·151		30	0·122
	20	0·120		40	0·093
	25	0·107	*m*-Nitrotoluene	25	0·0768
n-Butyl phenyl ether	20	0·110		35	0·0614
	25	0·100			

The solubility of hydrogen chloride in methyl and ethyl alcohols and in diethyl ether is much greater; the following values of the mol. fraction, N, are recalculated from data previously recorded (Mellor, II, 197).

Temperature °C.	-10	0	10	20	30
Methyl alcohol	0·513	0·480	-	0·437	0·398
Ethyl alcohol	-	0·512	0·484	0·467	0·437
Diethyl ether	0·549	0·529	0·470	0·402	0·328

In each case compound formation is responsible for these high values. Methyl alcohol forms the compound $HCl,MeOH$[92,93] (f.p. -65°), and dimethyl ether forms the two compounds HCl,Me_2O (f.p. -97°) and $4HCl,Me_2O$ (f.p. -103°).[92,94] The existence of compounds with acetone and diethyl ether is shown by the liquidus curves for these systems (Fig. 2).[95] In addition to the

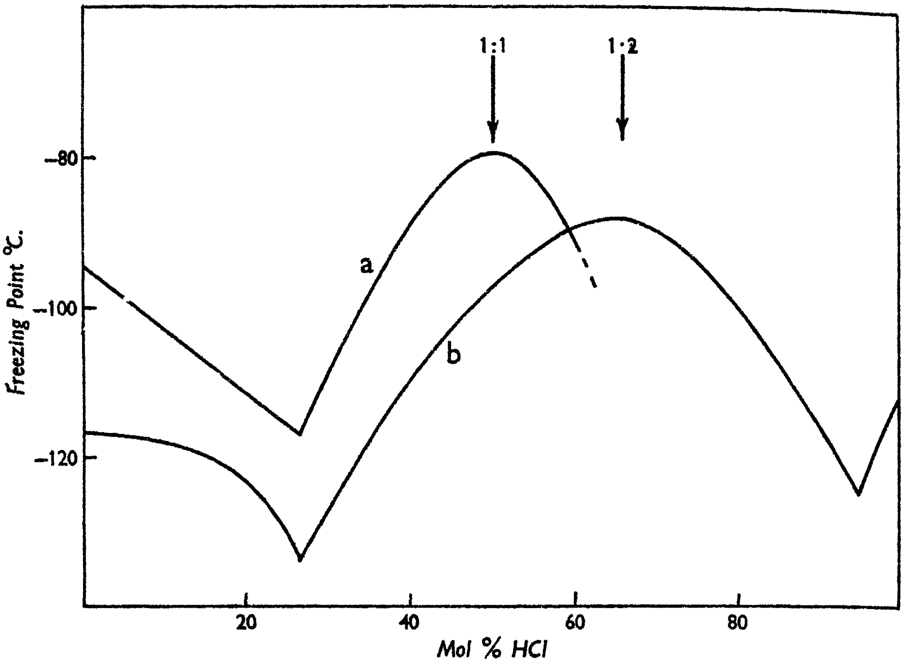

Fig. 2. LIQUIDUS CURVES FOR MIXTURES OF HYDROGEN CHLORIDE WITH (A) ACETONE (B) DIETHYLETHER

compounds shown in the figure, it has been suggested that the compound $5HCl,2COMe_2$ is also formed with acetone, and the compounds HCl,Et_2O and $5HCl,Et_2O$ with diethyl ether.[96] The more rapid decrease in the solubility in ether reflects the lower stability of this complex compared with that formed with the alcohols.

Measurements of the partial pressure of hydrogen chloride over its solutions in the non-aqueous solvents shown in Table XVII have confirmed that Henry's Law is obeyed, although the solutions show some departure from Raoult's Law. The table gives the Henry's Law constant *K* (atm./mol./1000 g. solvent) for a range of liquids at 25°.

TABLE XVII.- HENRY'S LAW CONSTANTS FOR HYDROGEN CHLORIDE IN NON-AQUEOUS SOLVENTS

Solvent	Molal concentration range studied (*m*)	*K*	Deviation from Raoult's Law	References
Benzene	0·014–0·273	2·04	-	97,104
Nitrobenzene	0·030–0·338	1·77	-	103
Acetic acid	0·030–0·34	0·347	-	97
o-Nitrotoluene	0·023–0·259	1·77	–ve	98
m-Nitrotoluene	0·012–0·139	1·65	–ve	98
Hexane	0·004–0·02	5·3	+ve	98
Toluene	0·015–0·137	2·09	–ve	99
Fluorobenzene	0·021–0·121	3·02	+ve	100

TABLE XVII (continued)

Solvent	Molal concentration range studied (m)	K	Deviation from Raoult's Law	References
Chlorobenzene	0·008 – 0·103	4·38	+ve	100
Bromobenzene	0·013 – 0·069	5·4	+ve	100
Iodobenzene	0·006 – 0·040	8·58	+ve	100
$\beta\beta'$-Dichloroethyl ether	0·009 – 0·571	0·94	–	90

Henry's Law (in the usual form $p = Km$) is not obeyed by solutions of hydrogen chloride in ethylene glycol.[97] When partial pressures for this solution are employed in the equation $p^{1/2} = K'ym$ (y = activity coefficient) used for aqueous solutions, K' has the value 0·02. The following values illustrate the variation of K with temperature.

	20°	30°	40°
Nitrobenzene[103]	1·59	2·08	2·51
Chlorobenzene[103]	–	4·65	5·71
Benzene[103]	–	2·33	2·91
$\beta\beta'$-Dichloroethyl ether[90]	0·82	1·03	1·40
Anisole[90]	0·97	1·21	1·54

The variation of mol. fraction solubility of hydrogen chloride (N) with temperature is expressed as $\log_{10}N = \Delta H/2{\cdot}303RT + \Delta S/2{\cdot}303R$. This has been used to determine the heat of solution ($-\Delta H$ g.-cal.) and the entropy of solution ($-\Delta S$ g.-cal./deg.). Values which have been established are recorded in Table XVIII.

TABLE XVIII. - HEAT AND ENTROPY OF SOLUTION OF HYDROGEN CHLORIDE

Solvent	$-\Delta H$	$-\Delta S$	Solvent	$-\Delta H$	$-\Delta S$
Carbon tetrachloride	3610[103]	–	Pentachloroethane	2200[89]	15·0[103]
	3530[90]		Diethyl ether	3840[103]	–
	3680[102]		Benzene	4300[103]	20·9[103]
Chloroform	3000[101]	–	Bromobenzene	4100[103]	–
Ethylene dichloride	3500[89]	18·4[103]	Chlorobenzene	4000[103]	20·7[103]
Ethylene dibromide	3200[89]	17·4[103]	Nitrobenzene	4000[103]	18·9[103]
sym.-Tetrachloroethane	3300[89]	18·4[103]	$\beta\beta'$-Dichloroethyl ether	3850[90]	16·9[90]
Trichloroethane	3600[89]	19·2[103]	Anisole	3870[90]	17·8[90]

The entropy values obtained from heats of solution have been correlated closely with infra-red absorption data. The thermodynamic and spectroscopic properties are related by the equation

$$\Delta S = 10{\cdot}0\Delta\mu - 21{\cdot}1$$

where $\Delta\mu$ represents the shift in the wave length of the $3{\cdot}46\mu$ absorption peak for gaseous hydrogen chloride on solution in the solvent.[90] In Table XIX the values of $-\Delta S$ determined thermodynamically are compared with values derived, using the above equation, from the shift in the infra-red absorption band.[91]

ELECTRICAL CONDUCTIVITY

The specific conductivity of liquid hydrogen chloride at −85° is $3{\cdot}5 \times 10^{-9}$ ohm^{-1} cm.$^{-1}$ The temperature coefficient is $-6{\cdot}5 \times 10^{-11}$ ohm^{-1}/degree.[105] The conductivity of solutions of hydrogen chloride in non-aqueous solvents is

TABLE XIX. - ENTROPY OF SOLUTION OF HYDROGEN CHLORIDE DETERMINED FROM THERMODYNAMIC AND SPECTROSCOPIC DATA

Solvent	$-\Delta H$	$-\Delta S$ (from thermodynamic data)	$-\Delta S$ (from infra-red data)
Phenetole	3950	17·6	17·7
n-Butyl phenyl ether	3780	17·2	17·3
Diphenyl ether	3800	18·9	19·0
m-Nitrotoluene	3900	18·8	18·7

largely determined by the extent to which the solvent molecule can serve as a proton acceptor;[106] the dielectric constant of the medium has a much smaller effect. Table XX illustrates the range of conductivities observed at 25°.

TABLE XX. - CONDUCTIVITY OF SOLUTIONS OF HYDROGEN CHLORIDE IN NON-AQUEOUS SOLVENTS

Solvent	Equivalent Conductivity	Dilution (litres containing 1 g.-equiv.)	Refs.
Methyl alcohol	196·7	∞	107,108,109
Ethyl alcohol	84·7	∞	107,108
n-Propyl alcohol	46·6	∞	110
n-Butyl alcohol	28·4	∞	111
*iso*Butyl alcohol	12·07	640	112
*iso*Amyl alcohol	2·15 (minimum)	-	113
Formic acid	75·0	∞	114
Acetic acid	0·0925	7,600	115
Nitromethane	0·233	11·1	116
Nitrobenzene	0·061	151	116
Diethyl ether	0·00053 (minimum)	-	117

As is usual in media of low dielectric constant, the conductivity passes through a minimum with increasing dilution. It is this minimum which is quoted above for *iso*amyl alcohol and diethyl ether. The specific conductivity of solutions in benzene, *cyclo*hexene, *cyclo*hexane and carbon tetrachloride is less than 7×10^{-13} ohm^{-1}.[118] The conductivity is increased by the addition of traces of water, particularly in the case of liquids of high dielectric constant.[116,117,119] Transport measurements on solutions of hydrogen chloride in anhydrous ethyl alcohol give a value of 0·71 for the hydrogen ion.[120] Some conductivity measurements on solutions of hydrogen chloride in fused salts (e.g. antimony chloride) have also been made.[121]

SOLID HYDROGEN CHLORIDE

Crystallographic studies have shown that solid hydrogen chloride has a molecular lattice. In accord with Pauling's theory of free rotation of molecules in crystals,[122] there is a clearly defined temperature above which the molecules rotate, and below which they only oscillate. In hydrogen chloride this results in dimorphism. At the transition temperature there is a sharp change in many of the physical properties of the solid. Those properties peculiar to solid transition will be discussed here; other changes have been treated under the appropriate physical property.

Heat capacity measurements give the transition temperature as 98·36°K.,[35] and 98·75°K.[39] Measurements of the change in dielectric constant of the solid support the former value.[81] The corresponding transition temperature for solid deuterium chloride is 105·03°K.[37] Calorimetric measurements of the heat of transition give values of 284·3[35] and 293·8[39] g.-cal./mol.; that for deuterium chloride is 320·1 g.-cal./mol.[37]

The crystal form which is stable above the transition point is cubic face-centred; the volume of the unit cell, measured at 100°K., is $162{\cdot}8 \times 10^{-24}$ c.c., corresponding to an axis of 5·46 A.,[3,4,5] in agreement with an earlier determination of 5·50 ± 0·05 A.[1] Below the transition temperature an orthorhombic face-centred form is stable. Its space group is V^7 or V_h^{23} $[D_2^7 - F_{222}$ or $D_{2h}^{23} - F_{mmm}]$. The lattice constants (measured at 100°K.) are $a = 5{\cdot}03$, $b = 5{\cdot}35$ and $c = 5{\cdot}71$ A.; the unit cell contains four molecules and has a volume of $154{\cdot}7 \times 10^{-24}$ c.c.[3] Both the above crystal forms are white. Under certain conditions of cooling it is possible to obtain a pink form also,[123] and the pink colour has been attributed to an unstable crystalline form of hydrogen chloride.[35] In these experiments the pink colour was observed only when condensation took place in a vacuum at the temperature of liquid air, the crystalline product being white when condensed in a bulb containing air. When the temperature of the pink solid was allowed to rise, the colour disappeared abruptly, and subsequent cooling did not restore it. These observations were independent of the method of preparation of the hydrogen chloride. The existence of a pink form of the solid has been refuted, the colour being attributed to the presence of traces of nitric oxide, which gives a coloured addition compound with hydrogen chloride.[124] The observation of the pink colour has, however, been reaffirmed in solid hydrogen chloride the purity of which was established by mass spectrographic analysis, and the colour is attributed to imperfections in the crystal lattice. Earlier work was confirmed by the observation that the appearance of the red form was dependent upon the rate of freezing (being obtained only on rapid freezing), and although the pink colour could be obtained in the complete absence of impurities, the addition of as little as 10^{-4} to 10^{-5} mol. fraction of nitric oxide intensified the colour.[125]

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THE PHYSICAL PROPERTIES OF HYDROCHLORIC ACID

SOLUBILITY AND SPECIFIC GRAVITY

Measurements of the solubility of hydrogen chloride additional to those previously given (Mellor,II,182) have been concerned with solution in various acids and acid-water mixtures (e.g. sulphuric and acetic acid) over a range of temperatures.[1-5] The influence of hydrochloric acid on the solubility in water of metal chlorides,[6-9] silica,[10] sodium fluosilicate[11] and hydrogen sulphide[12] has also been measured. Extensive details of the density of aqueous solutions of hydrochloric acid over wide ranges of temperature and concentration are given in International Critical Tables (Vol. III).[13] These values have been confirmed for dilute solutions and low temperatures, but it is believed that they are in error for higher temperatures and acid concentrations, and new values have been determined.[14] The equation $\phi = \phi^\circ + K\sqrt{M}$, where ϕ is the apparent partial molal volume and ϕ° is the partial molal volume at infinite dilution, is found to hold for hydrochloric acid;[14,15] the empirical constant K is much smaller than for other uni-univalent electrolytes.[14]

VISCOSITY AND COMPRESSIBILITY

The viscosity η of many electrolyte solutions (including hydrochloric acid) is related to the concentration C (mols./litre) by the formula:-

$$(\eta - \eta_0)\eta_0 = K_0 + K_1C^{1/2} + K_2C,$$

where η_0 is the viscosity of water. Measurements at 25° over the concentration range 0·02 to 1·4 M-hydrochloric acid give values for the constants K_0, K_1 and K_2 of 30, 620 and 8 respectively (each × 10^4).[16] The viscosities of aqueous solutions of hydrochloric acid containing sodium nitrate[17] and ethyl and methyl alcohols have also been determined.[18]

Careful measurements of the compressibility coefficient, β, of hydrochloric acid at 25°, using a piezometer, have given the values[19] in Table XXI.

TABLE XXI. - COMPRESSIBILITY COEFFICIENT OF HYDROCHLORIC ACID

Molar Concn.	Density	$10^6\beta$(atm.$^{-1}$)
0·5542	1·00704	41·93
1·1082	1·01623	41·22
2·2218	1·03370	40·17

The values were determined between 100 and 300 megabars, and are to be compared with the value (β,) 42·53 × 10^{-6} for pure water. There is a linear relationship between the apparent molal compressibility ($\beta V - \beta_1V_1$) and the square root of the concentration; V is the volume of solution containing 1 mol. of solute, and V_1 is the volume of water in which 1 mol. of solute is dissolved. An earlier determination at 18° gave similar values for β.[20] The velocity of sound in the solution, as a function of hydrochloric acid concentration, passes through a maximum at about 2M-HCl. The velocity at 22-29°C., measured by means of a supersonic interferometer at a frequency of 0·5 megacycles per second, is 1550 m. per sec.[21] A velocity of 1554 m. per sec. has been observed at 25° at a frequency of 2·75 megacycles per sec.[22] The compressibility has been determined from the velocity of sound, and is related to the concentration of hydrochloric acid by the expression:-

$$\beta = \beta_1 - K_1C + K_2C^{3/2}$$

where C is the molar concentration and K_1 and K_2 have the values 5·2 and 1·75 respectively.[21]

DISTRIBUTION BETWEEN WATER AND OTHER LIQUIDS

The distribution of hydrogen chloride between water and benzene, and between water and nitrobenzene, has been studied in attempts to determine the nature of the hydrogen chloride in these solvents.[23-25] The behaviour of hydrogen chloride in such systems depends upon its capacity to combine with the solvent and not on the dielectric constant of the solvent. Thus in water, hydrogen chloride is solvated, whereas in benzene and nitrobenzene it behaves as a normal undissociated solute. This is illustrated by the results[24] with benzene at 25° which are quoted in Table XXII.

TABLE XXII. - DISTRIBUTION OF HYDROGEN CHLORIDE BETWEEN WATER AND BENZENE

C_w	C_b	p_{HCl}	$p_{HCl}/C_b \times 10^3$
9·603	0·00213	2·95	1·39
10·215	0·00340	4·67	1·37
10·508	0·00423	5·72	1·35
11·43	0·00768	10·74	1·40
11·99	0·0110	15·6	1·42
12·93	0·0216	28·1	1·30

The concentrations C_w and C_b are in g. mols. per 1000 g. of solvent, and p_{HCl} is the partial pressure of hydrogen chloride over the aqueous solution. This partial pressure is nearly proportional to the concentration in the benzene layer (column 4), so that the behaviour of hydrogen chloride in benzene is quite normal. Table XXIII gives measurements of the distribution of hydrogen chloride between water and nitrobenzene.

TABLE XXIII. - DISTRIBUTION OF HYDROGEN CHLORIDE BETWEEN WATER AND NITROBENZENE

C_{water}	9·635	11·147	13·84	14·84	16·46	18·05	20·42
$C_{nitrobenzene}$	0·0027	0·0080	0·0396	0·0707	0·164	0·335	0·833

Measurements have been made of the distribution between water and a number of other liquids, for example methyl ethyl ketone, *n*-amyl and *n*-butyl alcohols, *sec.*-butyl alcohol and *tert.*-amyl alcohol[26] and phenol;[27] the change in the miscibility limits of *iso*amyl alcohol-water mixtures with variation in hydrogen chloride concentration has also been determined.[28]

DIFFUSION COEFFICIENTS

Diffusion coefficients for hydrogen chloride in aqueous solution have been determined from measurements of the rate of diffusion from one solution into a second, more dilute, solution through a porous (sintered glass) diaphragm. The simple law of diffusion of electrolytes was first derived by Nernst;[29] both positive and negative ions diffuse with the same velocity. It has been recognized that the diffusion coefficient D as defined by Fick's equation $dw = -D. \frac{dc}{dx}. dt$ (where dw is the quantity of electrolyte diffusing across 1 cm.^{2} in time dt under a concentration gradient dc/dx) is dependent to some extent upon the concentration of the electrolyte. It is necessary to distinguish between the apparent or integral diffusion coefficient D_1, and the true or differential coefficient D. D_1 is computed from an observed amount of solute diffusing per unit time from a higher concentration C_1 into a lower concentration C_2. This is related to D by the equation $D_1(C_1 - C_1) = \int_{C_2}^{C_1} D\mathrm{d}cl$ for small values of

$C_1 - C_2$, D is a linear function of concentration, so that $D = \bar{D}$, for a concentration $(C_1 + C_2)/2$.[30-32] Table XXIV shows the variation in the differential diffusion coefficient D (cm.^{2}/sec.) with concentration and temperature. C is the mean of the two concentrations employed (mols. HCl/litre) which differed by about 0·1 mol./litre.[30,31]

TABLE XXIV.- DIFFUSION COEFFICIENTS OF HYDROCHLORIC ACID IN WATER

C	Differential Diffusion Coefficient $D \times 10^5$			
	10°	15°	25°	35°
0	2·16	2·48	3·14	3·87
0·02	2·05	2·35	2·97	3·66
0·05	2·02	2·33	2·93	3·61
0·10	2·03	2·33	2·92	3·60
0·20	2·05	2·35	2·98	3·65
0·35	2·11	2·40	3·06	3·77
0·50	-	2·45	3·18	-
0·75	-	2·56	3·37	-
1·00	-	2·68	3·58	-

At each temperature the diffusion coefficient passes through a minimum at a concentration about 0·1 mol. HCl/litre. Hydrogen chloride has been used as diffusing solute in a number of studies concerned primarily with the development of diffusion techniques, and various values of D at selected temperatures and concentrations have been quoted.[33-37] The tangent to the log $D - \frac{1}{T}$ curve gives the activation energy of diffusion. Up to 0·2 molar hydrochloric acid, the energy is independent of acid concentration, being 4·4, 4·0 and 3·8 kg.-cal. for the temperature ranges 10 – 15°, 15 – 25° and 25 – 35° respectively. At higher concentrations the activation energy is dependent upon concentration; for the 15 – 25° temperature range the activation energies are 4·2, 4·4, 4·7 and 5·0 kg.-cal. for concentrations of 0·35, 0·50, 0·75 and 1·0 mols./litre respectively.[31] The rate of diffusion of ions through the gel structure has been proposed as the rate-determining step for anion exchange in ion-exchange resins; the energy of activation of the exchange reaction with hydrochloric acid is 6·6 kg.-cal.[38]

The diffusion coefficient is lower in alcohol-water mixtures than in water:[39] the values in Table XXV show the influence of ethyl alcohol concentration at 25°.

TABLE XXV.- DIFFUSION COEFFICIENTS OF HYDROCHLORIC ACID IN ETHYL ALCOHOL-WATER MIXTURES

EtOH (wt. %)	0	19	41	62·5	71	89	100
$D \times 10^5$ cm.^{2}/sec.	3·14	1·74	1·07	0·81	0·72	0·71	0·68

THERMAL DIFFUSION

The existence of a temperature gradient in aqueous solutions of hydrochloric acid quickly produces a concentration gradient.[40] Thermal diffusion has been studied by placing hydrochloric acid in the annulus between two concentric glass tubes, with reservoirs at top and bottom. The annulus used was approximately 94 cm. in length, and 0·15 cm. wide. The outer tube was maintained at 25°, and the inner tube at 76° by the use of boiling carbon tetrachloride. Under these conditions a stationary state is reached within 3 hours with hydrochloric acid; the equilibration period is even shorter for many other solutes, e.g. sulphuric acid and sodium chloride.[41] Table XXVI gives separation ratios for solutions of hydrochloric acid, alone and also containing other solutes.[42]

TABLE XXVI. - THERMAL DIFFUSION SEPARATION RATIOS FOR HYDROCHLORIC ACID SOLUTIONS

Solute	Ion	Separation Ratio after 1 hour
1N-HCl	H^+	1·195
	Cl^-	1·195
0·5N-HCl +	H^+	1·19
0·5N-H_2SO_4	Cl^-	1·21
	SO_4^{2-}	1·18
0·5N-HCl +	H^+	1·305
0·5N-NaCl	Cl^-	1·12
	Na^+	0·96
0·5N-HCl +	H^+	1·35
0·5N-NH_4Cl	Cl^-	1·12
	NH_4^+	0·90

The separation ratio is the concentration in the bottom reservoir divided by the concentration in the top reservoir. Using mixed solutes, it is found that the separation ratios of the components may be related to one another in any one of four ways: (1) they may be independent of one another, (2) they may both increase, (3) they may both decrease, or (4) one may increase and the other decrease. Solutions containing hydrochloric acid usually fall into category (1) (e.g. HCl-H_2SO_4 solutions) or (4) (e.g. HCl-NaCl or HCl-NH_4Cl solutions).[43] The thermal diffusion of electrolytes in mixed solutions has been related quantitatively to ionic mobilities, with good agreement between theory and experiment.[44] In a solution containing solutes AX and BX, then:-

$$R_a = R_{ax} + \frac{C_{bx}(u_b + u_x)(R_{ax} - R_{bx})}{C_{ax}(u_a + u_x) + C_{bx}(u_b + u_x)} \cdot \frac{u_a}{u_x}$$

where R_a, R_{ax} and R_{bx} are the separation ratios of ion A and the compounds AX and BX respectively, u is the mobility of the ion indicated by the suffix and C is the concentration. The 'negative effect', whereby the separation of certain electrolytes decreases in hydrochloric acid solutions (Table XXVI), is also predicted by the above equation, and is attributed to a kind of diffusion potential resulting from the difference in diffusion velocity between the ions.[45,46] The velocity of thermal diffusion in hydrochloric acid solutions is reduced to a half, or even less, by the addition of ethyl alcohol to the solution.[47]

BOILING POINT

Since the use of constant-boiling hydrochloric acid for analytical purposes was first suggested in 1909,[48] its use as a standard has increased widely, and the physical properties (particularly the composition) of the constant-boiling mixture have been determined with great accuracy. The rate of distillation influences the composition to some extent, and suitable experimental conditions for achieving the true mixture have been described.[49-53] The rate of approach to equilibrium during distillation has been measured;[54] starting with weak acid, equilibrium is attained more slowly than when starting with very strong acid. Physical properties of the constant boiling mixtures are given in Table XXVII for a wide range of pressures.[55-57]

TABLE XXVII. - PHYSICAL PROPERTIES AND COMPOSITION OF CONSTANT BOILING HYDROCHLORIC ACID

Pressure (mm. Hg)	Boiling Point °C.	Density/25°	Wt.-% HCl
50	48·724	1·1118	23·42
250	81·205	1·1042	21·883
400	92·080	1·1010	21·235
500	97·578	1·0993	20·916
600	102·209	1·0980	20·638
700	106·424	1·0966	20·360
760	108·584	1·0959	20·222
800	110·007	1·0955	20·155
1000	116·185	1·0933	19·734
1220	122·98	1·0915	19·358

These values (particularly the values at 760 mm.) have been confirmed,[58,59] and are accepted as being highly accurate. For analytical purposes, the variation in the composition of the constant boiling mixture has been studied over a narrow range of pressures near atmospheric pressure, and the results are given in Table XXVIII.[60]

TABLE XXVIII. - COMPOSITION OF CONSTANT BOILING HYDROCHLORIC ACID

Pressure (mm. Hg)	730	740	750	760	770	780
Wt.-% HCl	20·293	20·269	20·245	20·221	20·197	20·173

As would be expected, these solutions are very stable; samples of constant-boiling hydrochloric acid prepared by distillation have been found, after storage for more than three years, to differ in composition by less than 0·1% from freshly prepared samples.[49] Whether the addition of a third component influences the maximum boiling point and the corresponding composition depends upon the nature of the compounds formed in solution.[61] Thus, an addition of ammonium chloride or lithium chloride does not alter the maximum boiling point but lowers the concentration of hydrochloric acid at which the maximum boiling point occurs. Both zinc chloride and ferric chloride form addition compounds with hydrogen chloride, and these salts lower the maximum boiling point and the hydrochloric acid concentration. On the other hand, added sulphuric acid raises the maximum boiling point and also increases slightly the corresponding hydrochloric acid concentration.

VAPOUR PRESSURE

The values for the partial pressure of hydrogen chloride over its aqueous solutions previously given (Mellor,II,189) were obtained by passing air over the surface of hydrochloric acid in saturators, and determining the amount of hydrogen chloride in the saturated air. By this method it was not possible to make accurate determinations for hydrochloric acid solutions below 3 molar because of the minute quantities of hydrogen chloride contained in the vapour phase. Using the method of distillation under reduced pressure, however, it has been possible to collect larger quantities of the vapour phase and thus to extend the measurements to concentrations as low as 0·3 molar. In obtaining the values given in Table XXIX, the distillate was analysed by measurement of its conductivity.[62]

TABLE XXIX. - VAPOUR PRESSURE OF HYDROCHLORIC ACID AT LOW CONCENTRATIONS (25°)

Molar concn. of HCl	0·345	0·46	0·654	1·11	1·57	2·4	4·2	5·31
Partial pressure of HCl (mm. Hg)	$3{\cdot}2 \times 10^{-6}$	$5{\cdot}62 \times 10^{-6}$	$1{\cdot}17 \times 10^{-5}$	$4{\cdot}03 \times 10^{-4}$	$9{\cdot}77 \times 10^{-4}$	$3{\cdot}24 \times 10^{-3}$	0·0255	0·082

Where the concentration ranges overlap (3·5 – 5·3 M.) these values are about 15% higher than those previously reported. At higher temperatures the partial pressures are still almost negligible; for example, at 50° p_{HCl} for a 4·66M. solution does not exceed 1 mm.[63] Other values have been obtained which, though differing a little from those in Table XXIX, confirm the very small partial pressure of hydrogen chloride in dilute solutions.[64-66] At high concentrations, however, the partial pressure is considerable. Table XXX shows some selected values.[67]

TABLE XXX. - VAPOUR PRESSURE OF HYDROCHLORIC ACID AT HIGH CONCENTRATIONS (25°)

Molar concn. of HCl	13·65	16·41	20·27	21·05	22·22
Partial pressure of HCl (mm. Hg)	1·54	12·90	166·0	272·3	515·0

The change in vapour pressure with concentration reflects the change in the state of hydrogen chloride in aqueous solution. In dilute solutions, ionization is complete; the hydrogen chloride is present as the hydrated ions, and the infra-red absorption bands characteristic of the HCl molecule are absent.[68] In very concentrated solutions, the large partial pressures indicate that much of the hydrogen chloride is present in the form of undissociated HCl molecules.

Partial pressure measurements on concentrated hydrochloric acid solutions containing added salts have been applied to the study of compound formation in those solutions.[68] The addition of cuprous chloride lowers the partial pressure, and comparison with solutions of pure hydrochloric acid having the same partial pressure shows that the compound HCl,2CuCl is present in solution. Ammonium chloride increases the solubility of hydrogen chloride, and lowers the partial pressure. But when both cuprous chloride and ammonium chloride are added, in 1:2 molecular ratio, to concentrated hydrochloric acid, a compound, $2NH_4Cl,CuCl$, is formed which does not influence the behaviour of hydrogen chloride, and the partial pressures are identical with those for pure hydrochloric acid of the same concentration. Titanium tetrachloride, lithium chloride, stannous chloride and stannic chloride increase the partial pressure. The influence of added cupric chloride on the partial pressure of hydrochloric acid varies with the concentration of the salt. In solutions containing 2 mols. $CuCl_2$ per 100 mols. of water, the partial pressure is not altered; at lower cupric chloride concentrations the partial pressure is decreased, and at higher concentrations it is increased.

THERMODYNAMIC PROPERTIES

HEAT OF SOLUTION

The heat of solution of hydrogen chloride in water has been determined over the temperature range 3·6 to 62·3°. At 21·5°, and over the concentration range *m* = 0·006 to 1 (where *m* = mols. of hydrogen chloride per 1000 g. of water) the heat of solution Q has been represented by the formula $Q_m = 17{\cdot}77 - 0{\cdot}4515m^{\frac{1}{2}}$.[69] Later determinations carried out at 21°[70] and 19°[71] have given values not quite in agreement with the above formula, since the heat of solution when plotted against $m^{\frac{1}{2}}$ passes through a flat maximum and then shows a slight fall (see Table XXXI below). These results give a value of 17·45 to 17·50 kg.-cal. per mol. for the heat of solution at infinite dilution and at 21°,[70] compared with an earlier determination of 17·88 kg.-cal. per mol. at 25°.[72]

TABLE XXXI. - HEAT OF SOLUTION OF HYDROGEN CHLORIDE IN WATER

m	Q_m at 21°[70]	m	Q_m at 19°[71]
0·0949	17·64	0·00564	17·61
0·0835	17·67	0·00460	17·60
0·0631	17·71	0·00257	17·56
0·0337	17·74	0·00204	17·50
0·01613	17·71	0·00113	17·57
0·0121	17·71	0·000783	17·56
0·0058	17·66	0·000427	17·50
		0·000215	17·22

Heats of solution in methyl alcohol-water mixtures have also been measured, and are given in Table XXXII.[73]

TABLE XXXII. - HEAT OF SOLUTION OF HYDROGEN CHLORIDE IN METHYL ALCOHOL AND METHYL ALCOHOL-WATER MIXTURES

Wt. % CH_3OH	0	20·86	44·18	76·0	100
Heat of solution at 25°(kg.-cal./mol.)	17·88	17·28	17·00	18·40	19·70

The heat evolved passes through a minimum at about 15% methyl alcohol, an effect also observed for solutions of the chlorides of sodium, potassium, rubidium and cæsium.

HEAT OF DILUTION

Some values for the integral heats of dilution of hydrogen chloride in water are given in Table XXXIII,[74] where N is the ratio of mols. of water to mols. of hydrogen chloride present.

TABLE XXXIII. - HEATS OF DILUTION OF HYDROCHLORIC ACID

N_1	→ N_2	Temp. °C.	Heat of dilution (kg.-cal./mol.)
10·058	200	20	+1·136
10·184	200	20	1·121
10·309	200	20	1·109
3·213	3·223	20·5	0·013

Much of the heat change on dilution results from changes in ionic hydration. Measurements over the 20°– 70° temperature range have shown that the heat of dilution-concentration curve is little influenced by temperature.[75] The relation between heat of dilution and temperature is almost linear for concentrations up to 15 wt.-%, but at higher concentrations (25%) a minimum appears in the curve at about 60°. Data on heat of dilution have been used extensively in the determination of the apparent and partial relative molal heat contents of both solute and solvent in hydrochloric acid solutions at 25°. The apparent relative molal heat content of hydrochloric acid ($\Phi_H - \Phi_H^0$) is given by the expression:-

$$\Phi_H - \Phi_H^0 = \frac{1997m^{1/2}}{1 + 1{\cdot}123m^{1/2}} + 747m$$

for concentrations up to $m^{1/2} = 1{\cdot}2$ ($\underline{m}$ = mols. HCl per 1000 g. H_2O).[76-78] For the temperature range 18–25°, assuming $\Phi_H^0 = +32{\cdot}5$, the simpler relation $\Phi_H - \Phi_H^0 = Am^{1/2}$ may be applied, where $A = 7{\cdot}2$. The partial molal heat capacity of solute and solvent are thus linear functions of $m^{1/2}$ and $m^{3/2}$ respectively.[79-82] If $\bar{C}_{p_2}$ and $\bar{C}_{p_1}$ are the partial molal heat capacities of hydrochloric acid and water respectively, then:-

$$\bar{C}_{p_2} - \bar{C}_{p_2}^0 = \frac{3}{2}Am^{1/2}, \text{ and } \bar{C}_{p_1} - \bar{C}_{p_1}^0 = \frac{Am^{3/2}}{2\,(55{,}508)}$$

SPECIFIC HEAT

The values given in Table XXXIV were determined using an adiabatic twin calorimeter.[80]

TABLE XXXIV. - SPECIFIC HEAT OF HYDROCHLORIC ACID SOLUTIONS (25°)

Molar Concn.	C_p	Molar Concn.	C_p
0·0100	0·99950	0·1629	0·98966
0·0400	0·99764	0·2552	0·98420
0·0626	0·99614	0·8100	0·95182
0·0900	0·99426	2·0112	0·89019

These values agree well with separate determinations at 18° and a somewhat higher concentration range;[81] other values which have been reported are appreciably lower.[82,83]

HEAT OF NEUTRALIZATION

Calculated values for the heat of neutralization of hydrochloric acid by sodium hydroxide[84] are in good agreement with previous values determined calorimetrically;[85,86] at infinite dilution the heat of neutralization is 13,650 g.-cal./mol. Other values are given in Table XXXV.[86]

TABLE XXXV. - HEAT OF NEUTRALIZATION OF HYDROCHLORIC ACID BY STRONG BASES

Base	Heat of neutralization for HCl, 100 H_2O at 20° (g.-cal.)	Temperature coefficient (g.-cal./degree)
LiOH, 100 H_2O	14,014	−55·4
NaOH, 100 H_2O	13,895	−52·7
KOH, 100 H_2O	13,993	−48·4

The heat of neutralization of hydrogen chloride by sodium methoxide in methyl alcohol solution falls, with increasing dilution, to a greater extent than in water;[87] the limiting value of 11,200 g.-cal. is identical with that obtained for the heat of neutralization of hydrogen chloride by sodium ethoxide in ethyl alcohol solution.[88] The heat of neutralization of hydrogen chloride by two weak bases is given in Table XXXVI.

MOLAL VOLUME

A linear relation, $\phi = \phi_0 + km^{1/2}$, exists between the apparent partial molal volume of hydrochloric acid (ϕ) and the square root of the molal concentration

TABLE XXXVI. - HEAT OF NEUTRALIZATION (g.-cal./mol.) OF HYDROGEN CHLORIDE BY WEAK BASES IN VARIOUS MEDIA

	In H_2O	In Methyl Alcohol	In Ethyl Alcohol
Ammonia	12,300[87]	17,630[87]	17,854[89]
Aniline	7,500[87]	9,930[87]	-

(m). Using this relation, the molal volume at infinite dilution (ϕ_0) has been derived by extrapolation of values for 5 to 16 m. solutions;[90] the variation with temperature t (°C.) is given by the expressions:-

$$\phi_0 = 16{\cdot}401 + 0{\cdot}08571t - 0{\cdot}0009016t^2$$
$$K = 0{\cdot}9461 - 0{\cdot}01066t + 0{\cdot}0001666t^2$$

In Table XXXVII, values of the apparent molal volumes of hydroxonium chloride at infinite dilution (obtained by adding to the value for hydrogen chloride the volume of 1 mol. of water at corresponding temperature) is compared with the molal volume of two molecules of water.[91]

TABLE XXXVII. - MOLAL VOLUMES OF HYDROXONIUM CHLORIDE

t°C.	ϕ(2 mols. H_2O)	$\phi(H_3O.Cl)$	t°C.	ϕ(2 mols. H_2O)	$\phi(H_3O.Cl)$
0	36·04	34·3	30	36·19	36·2
10	36·04	35·3	40	36·31	36·4
20	36·10	35·9	50	36·47	36·5
25	36·14	36·2	60	36·65	36·4

The apparent molal volume of many electrolyte mixtures containing hydrochloric acid, in aqueous solution, varies linearly with $m^{1/2}$ as for pure hydrochloric acid, provided the concentration is above 0·03m.[92] For aqueous solutions containing sodium chloride and hydrochloric acid, the partial molal volume of the hydrochloric acid is increased (maintaining constant total concentration) by increase in the sodium chloride content, the increase being a linear function of the sodium chloride concentration.[93] The apparent and partial molal volumes of deuterium chloride at higher concentrations differ only slightly from corresponding values for hydrogen chloride.[94]

ACTIVITY COEFFICIENTS

The activity coefficient for hydrochloric acid in water has been determined with great accuracy over a wide temperature range. The values have been established from cell measurements with[95,96] and without[97-100,105] liquid junction, from vapour pressure data[100] and from the depression of the freezing point.[100-102] The values given in Table XXXVIII were determined by careful measurements of the e.m.f. of the cell $H_2|HCl\,(M)\,|\,AgCl|Ag$.[98,103,104] The value of $\gamma\pm$ falls as the temperature increases; at any one temperature the value $\gamma\pm$ passes through a minimum at about 0·5 molar concentration.

The values at lower concentrations agree well with earlier determinations by freezing point measurements.[100] The assumptions made in the calculation of activity coefficients at low concentration are not fully applicable when an appreciable proportion of the water present is used to solvate the solute ions; this accounts for the very high values of γ observed at high concentrations. The variation in activity coefficient in the presence of another electrolyte, at constant total concentration, has been followed using cells of the type $H_2|HX(m_1)$, $MX_n(m_2)|AgX-Ag$, where $m_1 + m_2$ is constant. There is a linear relation between the logarithm of the mean activity coefficient and the concentration of hydrochloric acid in the presence of lithium, sodium, potassium

TABLE XXXVIII. - MEAN ACTIVITY COEFFICIENT ($\gamma\pm$) OF HYDROCHLORIC ACID IN WATER

Molar concn. M	Mean activity coefficient $\gamma\pm$			
	0°	20°	40°	60°
0·0001	0·9890	0·9892	0·9885	0·9879
0·0005	0·9756	0·9759	0·9741	0·9734
0·002	0·9541	0·9527	0·9505	0·9491
0·005	0·9303	0·9294	0·9265	0·9235
0·01	0·9065	0·9052	0·9016	0·8987
0·05	0·8346	0·8317	0·8246	0·8168
0·1	0·8027	0·7985	0·7891	0·7813
0·5	0·7761	0·7616	0·7432	0·7237
1·0	0·8419	0·8162	0·7865	0·7541
2·0	1·078	1·024	0·9602	0·9072
3·0	1·452	1·345	-	-
4·0	2·006	1·812	-	-
5	2·771	2·431	2·118	-
10	14·66	11·21	8·523	-
15	56·70	37·76	24·98	-

and cæsium chlorides[106] and calcium, strontium and barium chlorides;[107,113] at total concentrations up to 3 molar. The linear relation has been shown to persist up to total concentrations of 6 molar in the case of uni-univalent electrolytes;[108] it has been observed to hold also for salts lacking a common ion, such as sodium and potassium perchlorates.[109] Similar results have been obtained for the variation in activity coefficient of solutions of hydrochloric acid containing aluminium chloride,[110] cerous chloride,[111] perchloric acid and sodium dithionate.[112]

Many measurements of the activity coefficient of hydrochloric acid in mixtures of water with other liquids have been made. The most extensive investigation has been carried out with water-dioxan mixtures, and from results in dilute solution the increase in ionic association with decrease in dielectric constant has been observed. The results have been considered in the light of the Debye-Hückel Limiting Law, $-\log\gamma\pm = Az_+z_-u^{1/2}$; where z_+ and z_- are the valencies of the ions, u is the ionic strength and A is constant. In water alone, the activity coefficients lie above the straight line representing this limiting law. As the dielectric constant is decreased by addition of dioxan, the activity coefficients approach the limiting law values, and in 70% dioxan the activity coefficient-concentration curves are superimposed for hydrochloric acid concentrations below 0·002 M. At higher dioxan concentrations (82%) the activity coefficient for these dilute solutions of hydrochloric acid falls below the Debye-Hückel line. The coefficient has been measured over a temperature range 0 - 50°; at all concentrations it decreases with increasing temperature, showing that the relative partial molal heat content is always positive.[114] Table XXXIX gives values at 25°.

Activity coefficients of hydrochloric acid have also been determined in mixtures of water with methyl,[115] ethyl,[116-120] and *iso*propyl[116] alcohols, glycerol,[120,121] acetic acid[123] and acetone,[124] and in pure methyl[122] and ethyl[117,120] alcohol. The general form of this function is similar to that for aqueous solutions. The measurements have been extended to mixed solvents containing added salts; activity coefficients of hydrochloric acid have been determined from 0° to 50° in methyl alcohol-water mixtures containing sodium chloride, maintaining a constant ionic strength of unity. $\log\gamma_{HCl}$ was found

TABLE XXXIX. - MEAN ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN DIOXAN-WATER MIXTURES AT 25°

Molar concentration M.	0·005	0·01	0·05	0·1	0·5	1·0	1·5	3·0
% dioxan								
20	0·896	0·862	0·763	0·720	0·660	0·704	0·786	1·219
45	0·808	0·753	0·607	0·547	0·465	0·497	0·570	1·001
70	0·505	0·418	0·258	0·212	0·163	0·187	0·240	-
82	0·218	0·163	0·0826	0·0634	0·0504	-	-	-

to vary linearly with acid concentration, and the slope of the curves is independent of alcohol concentration within the range 10 – 60 wt.-% of alcohol.[125]

MAGNETIC SUSCEPTIBILITY

The specific and molar susceptibilities of hydrochloric acid are $-0{\cdot}602 \times 10^{-6}$ and $-22{\cdot}0 \times 10^{-6}$ c.g.s. units respectively.[126-130] It was claimed that the mass susceptibility of solutions of hydrochloric acid showed well-defined maxima and minima with variation in concentration, occurring in most cases at concentrations corresponding to stoicheiometric hydrates.[126] Repetition of this work, particularly over the concentration range $HCl,8H_2O$ to $HCl,12H_2O$, where the greatest variations in susceptibility had been found, indicated no maxima or minima, a linear relation being observed between acid concentration and mass susceptibility of the liquid.[127,130] It follows from this that the susceptibilities of the solute and solvent are additive. Measurement of the magnetic rotation of plane-polarized ultra-violet light (3441 – 3632 A.) in aqueous solutions of hydrochloric acid has shown that the angle of rotation decreases with increasing concentration.[131] Using values for the magneto-optical rotations for the *D* line, the molecular rotation for hydrogen chloride in water is $3{\cdot}31 \times 10^{-10}$, and $2{\cdot}14 \times 10^{-10}$ min. sq. cm. for the dissociated and undissociated forms respectively.[132]

SURFACE PROPERTIES

Most inorganic salts increase the surface tension of water, irrespective of the valency of the ions involved. However, the hydrogen ion may be selectively adsorbed, so that some acids, such as hydrochloric and nitric acids, lower the surface tension.[133] Ammonium hydroxide is also among the few inorganic compounds which show this property; sodium and potassium hydroxides increase the surface tension. The lowering of surface tension by hydrochloric acid is small, so that different experimental determinations are not in very close agreement. Selected values from available data are given in Table XL.

The values assumed for the surface tension of water at 20° were 72·75 dynes/cm. (col. 2), and 72·69 dynes/cm. (col. 3) and at 25°, 72·01 dynes/cm. (col. 4). These results have been discussed in the light of theories of ion adsorption at liquid surfaces.[136] On extending the measurements to very low concentrations, the surface tension values have been found to pass through a maximum, as shown in Table XLI, and at concentrations below 0·3 molar the surface tension is slightly greater than that of pure water.[137] Since the differences are slight, the tensions are expressed as fractions of the value for pure water.

As the temperature is increased, the extent to which the surface tension of hydrochloric acid falls below the water value ($-\Delta\gamma$) is diminished. Thus, $\Delta\gamma$ at 0° is five times as large as $\Delta\gamma$ at 20°. At 40°, $\Delta\gamma$ becomes positive for

TABLE XL.- SURFACE TENSION OF HYDROCHLORIC ACID SOLUTIONS

Molar concentration	Lowering of surface tension ($\gamma_{H_2O} - \gamma_{soln.}$) dynes/cm.		
	20°[134]	20°[135]	25°[136]
0·5	0·2	-	-
1·0	0·3	-	0·14
1·048	-	0·17	-
2·0	0·5	-	-
2·096	-	0·39	-
3·0	-	-	0·37
3·668	-	0·69	-
4·0	0·9	-	-
4·716	-	0·89	-
5·0	-	-	0·58
5·764	-	1·17	-
6·0	1·3	-	-
6·812	-	1·52	-
9·0	2·2	-	-
9·435	-	3·07	-
10·48	-	3·98	-
17·7	7·0	-	-

TABLE XLI.- SURFACE TENSION OF DILUTE HYDROCHLORIC ACID SOLUTIONS (25°)

Molar concentration	$\gamma_{soln.}/\gamma_{H_2O}$
0·00075	0·99970
0·00442	0·99987
0·0222	0·99998
0·052	1·00000
0·1022	1·00034
0·1559	1·00012
0·5146	0·99933

solutions up to 8·5M. concentration, passing through a maximum at about 4M.[138] In the presence of an added salt, the surface tension is not a mean of the values for the separate solutions, and hydrochloric acid lowers the surface tension of salt solutions much more than it lowers the tension of water. This effect increases with salt concentration, and has been confirmed for a range of salts.[136,138,139] The magnitude of this effect is illustrated in Table XLII.

TABLE XLII.- SURFACE TENSIONS OF HCl + NaCl SOLUTIONS AT 25°

Molar concentration HCl	Molar concentration NaCl	$\Delta\gamma$
1·0	-	-0·14
1·0	0·99	+1·11
1·0	2·95	+3·41
1·0	4·96	+5·56
-	1·021	+1·75
-	4·360	+7·42

Little information is available on the interfacial tensions between hydrochloric acid and immiscible liquids. At the hydrochloric acid–benzene interface, the interfacial tension passes through a maximum value at pH 5.[140]

Solutions of hydrochloric acid, even at extreme dilution, have a lower interfacial tension against mercury than has water. This is one of the properties influencing the rate at which a drop of the solution spreads on a mercury surface.[141]

Much work has been carried out on the adsorption of hydrochloric acid from aqueous solution to the surface of charcoal. The results of these measurements are not recorded here, since the degree of adsorption depends to a large extent on the condition of the charcoal. Thus, the adsorption has been compared using charcoals from different sources,[142-144] and of differing ash content.[145] The presence of oxide films produced by preheating the charcoal in oxygen at various temperatures and pressures influences the adsorption to a marked degree,[146-149] as does activation of the charcoal by platinum, hydrogen[150] and nitrogen.[151] The results of these measurements are primarily of interest in the study of adsorption mechanisms.[152-157] Adsorption isotherms have been derived for hydrochloric acid solutions containing added electrolytes;[158-160] measurements of adsorption from solutions in aqueous methyl alcohol, ether and acetone show that the presence of these organic compounds decreases the adsorption of hydrogen chloride by activated charcoal.[161] Adsorption in hydrochloric acid solutions has also been studied using silica,[162] hydrated stannic oxide,[163] aluminium oxide gel and ferric oxide gel.[164]

Electro-kinetic properties have also been investigated, particularly for the glass–hydrochloric acid interface. When the two phases are brought into contact, there is set up an electrical double layer which is believed to be in two parts. One, the Helmholtz plane parallel double layer, has approximately the thickness of a single ion, and is fixed at the solid interface. The other, the electrokinetic (or zeta-) potential, is diffuse and extends some distance into the liquid, and is thus the potential between the boundary of the fixed part of the double layer and a point far in the bulk of the liquid. The zeta-potential (ζ) may be measured from the streaming potential (S) which is set up on passing the liquid through a capillary tube; the two are related by the equation $4\pi\eta KS = \zeta PD$, where P is the driving pressure, D the dielectric constant, η the viscosity and K the specific conductivity of the liquid. The zeta-potential for the glass-water interface is near 0·05 volt. In common with many other acids, hydrochloric acid makes this potential more positive. In appreciable concentration (above 2×10^{-5} mol./l.) the zeta-potential is near 0·09 volt and is not greatly influenced by concentration.[165,166] At high dilution the observed values vary with the dimensions of the apparatus used, since surface conduction is not then negligible.[166,167] Zeta-potentials for hydrochloric acid at other solid surfaces have also been derived, for example, from measurement of endosmosis rates through diaphragms of powdered carborundum.[168]

ELECTRICAL CONDUCTIVITY

The study of the electrochemistry of hydrochloric acid in water, non-aqueous solvents and their mixtures is probably more comprehensive than that for any other electrolyte. The results have been applied in the evaluation of the various constants involved in the application of the Debye–Hückel–Onsager theories of solution, and in the study of ionic dissociation and inter-ionic attraction.[169] Much of the work has been concerned with dilute solutions, and the most accurate measurements of conductivity have been carried out at 25°[170,171] Some typical data are given in Table XLIII.

In very dilute solution the $\Lambda - c$ relation follows the limiting slope of the Onsager equation:-

$$\Lambda_v = \Lambda_\infty - (A + B\Lambda_\infty)\, C^{1/2}$$

TABLE XLIII. - EQUIVALENT CONDUCTIVITY OF DILUTE SOLUTIONS OF HYDROCHLORIC ACID AT 25°

concn. g. equivs./l.	0	0·0005	0·001	0·005	0·01	0·02	0·05	0·1
Λ_v	426·16	422·74	421·36	415·80	412·00	407·24	399·09	391·32

for conductivity in aqueous solutions of 1:1 electrolytes. The constants A and B are temperature-dependent, and vary from $A = 29{\cdot}47$, $B = 0{\cdot}2198$ at 0° to $A = 116{\cdot}98$, $B = 0{\cdot}2461$ at 60°.[169] Deviations from this limiting slope occur at higher concentrations; the curves show two points of inflexion, which are near 0·25 and 3·5M. at 60°, and move to lower concentrations as the temperature is decreased. At the highest concentrations the proton-exchange mechanism, which is responsible for the high mobility of the hydrogen ion, is influenced by proton-chloride ion combination,[171] as is indicated in Table XLIV.

TABLE XLIV. - INFLUENCE OF TEMPERATURE AND CONCENTRATION ON THE EQUIVALENT CONDUCTIVITY OF HYDROCHLORIC ACID

c (gram equivs. per litre)	Equivalent conductivity Λ			
	5°	25°	45°	65°
0	297·6	426·2	550·3	666·8
0·25	266·2	377·4	482·8	578·2
1·0	235·2	332·3	424·9	509·2
2·25	192·0	270·0	346·1	416·3
4·0	143·5	200·1	256·9	310·8
6·25	97·9	134·7	172·5	209·5
9·0	61·3	83·5	106·6	130·0

The absolute change in conductivity with concentration or with temperature is decreased in the most concentrated solutions; temperature coefficients are given in Table XLV.

TABLE XLV. - TEMPERATURE COEFFICIENT OF EQUIVALENT CONDUCTIVITY

$$\frac{100}{\Lambda}\left(\frac{d\Lambda}{dT}\right)_c$$

c gram equivs. per litre	Temp. coefficient			
	5°	25°	45°	65°
0	2·18	1·49	1·10	0·85
0·25	-	1·44	1·04	-
1·0	-	1·42	1·05	-
2·25	-	1·43	1·06	-
4·0	-	1·42	1·08	-
6·25	-	1·40	1·09	-
9·0	-	1·36	1·10	-

The variation in ionic mobilities with temperature shown in Table XLVI has also been determined from the above data and the corresponding transport numbers.[171,172]

The absolute temperature coefficient $(\delta\lambda_0/\delta T)_c$ of mobility of the chloride ion is seen to increase with temperature, which is contrary to the behaviour of the hydrogen (and many other) ions.

The cation transport numbers in hydrochloric acid have been determined

TABLE XLVI. - LIMITING IONIC MOBILITIES AND THEIR TEMPERATURE COEFFICIENTS IN HYDROCHLORIC ACID

Temp. °C.	λ_0		$\frac{100}{\lambda_0}\left(\frac{d\lambda_0}{dT}\right)_c$	
	H^+	Cl^-	H^+	Cl^-
5	250·6	47·0	2·02	2·99
15	300·9	61·2	1·65	2·39
25	349·9	76·3	1·37	2·05
35	396·7	92·5	1·15	1·80
45	440·8	109·5	0·97	1·60
55	482·1	127·4	0·83	1·44
65	520·8	146·0	0·72	1·31

using electromotive force measurement,[172] and the moving boundary method.[173] The close agreement is shown in Table XLVII.

TABLE XLVII. - CATION TRANSPORT NUMBER OF HYDROCHLORIC ACID AT 25°

c gram equivs. per litre	0·005	0·01	0·02	0·05	0·10
t_+ (moving boundary)	0·8239	0·8251	0·8266	0·8292	0·8314
t_+ (e.m.f.)	0·824	0·825	0·827	0·830	0·832

From electromotive force measurements, the variation of this transport number with temperature, shown in Table XLVIII, has been determined over a wider concentration range.[172]

TABLE XLVIII. - INFLUENCE OF TEMPERATURE ON CATION TRANSPORT NUMBER IN HYDROCHLORIC ACID

c gram equivs. per litre	0·01	0·1	1·0	2·0	3·0
t_+ 5°	0·845	0·850	0·855	0·857	0·858
15°	0·835	0·840	0·848	0·849	0·850
35°	0·816	0·823	0·833	0·835	0·836
45°	0·806	0·814	0·824	0·826	0·827

In order to study the influence of dielectric constant and similar properties of the solution on the degree of ion association, the electrical conductivities of hydrochloric acid have been determined in mixtures of water with a wide range of organic liquids. Some values are collected in Table XLIX.[174]

Detailed measurements covering a range of conditions have been made for solutions in mixtures of water with methyl alcohol,[176] ethyl alcohol,[175,177,178] acetone[177,179] and glycerol.[177,180] As with solutions in pure water, the equivalent conductivity of hydrochloric acid in mixtures of water with organic solvents also increases considerably with increase in temperature. This is illustrated in Table L.[181]

For the two lower dioxan concentrations, the experimental data follow closely the Onsager limiting slope; in 70 and 82% dioxan ion association is pronounced.

Many other investigators have contributed to our present knowledge of the electrochemistry of hydrochloric acid; reference should be made to work on electrical conductivity,[182-184] ionic mobility,[185-188] cataphoresis,[189] and transport numbers[190-195] in pure hydrochloric acid solutions, and in solutions containing

TABLE XLIX. - EQUIVALENT CONDUCTIVITY OF 0·1N-HCl IN ORGANIC SOLVENT-WATER MIXTURES AT 25°

Volume % organic solvent	10	30	50	70	90
Methyl alcohol	337·5	235·1	163·7	111·7	73·5
Ethyl alcohol	320·3	205·7	127·2	75·5	34·7
Glycol	326·2	204·8	118·4	56·4	21·4
Glycerol	321·8	185·1	87·0	27·9	4·5
Acetone	431·7	241·0	161·0	92·6	21·5
Dioxan	329·1	221·9	128·7	50·3	10·8
Formic acid	370·3	282·1	188·0	115·8	64·2
Acetic acid	332·1	210·7	116·6	52·6	14·9
n-Propanol	324·7	210·7	128·7	64·06	20·42

TABLE L. - INFLUENCE OF TEMPERATURE ON THE EQUIVALENT CONDUCTIVITY OF HYDROCHLORIC ACID IN DIOXAN-WATER MIXTURES

% Dioxan	Equiv. conductivity at infinite dilution Λ_∞			
	15°	25°	35°	45°
20	250·7	302·7	354·2	406·0
45	146·7	180·2	216·5	253·6
70	74·5	93·1	112·4	131·9
82	47·2	57·5	69·6	88·3

also sodium chloride and potassium chloride.[196] The addition of hydrophilic colloids (e.g. gelatin, gum arabic, salep, dextrin) to hydrochloric acid solutions reduces the transport number of the hydrogen ion; the colloid forms a complex with the cation, reducing its velocity; the conductivity of the solution is also reduced.[197,198] Sucrose has a similar effect, and the decrease in conductivity is proportional to the sucrose content of the solution.[199] The transport number of the chloride ion remains constant in hydrochloric acid solutions containing up to 30 wt.-% of sucrose, but is decreased at higher sucrose concentrations.[200] The decrease in conductivity is attributed to changes in viscosity, ion hydration and ion mobility, variation in dielectric constant being a relatively unimportant factor.[199]

Electrical conductivities have been studied employing physical conditions (e.g. high frequency[201] and high potential direct current[202]) differing from those normally employed in conductivity measurement. Early observations on the change in electrical conductivity with pressure, over a range up to 3000 kg./cm.^{2} (Mellor,II,194) have been extended[203] to pressures as high as 11000 kg./cm.^{2} Typical results are given in Table LI where Λ_p represents the equivalent conductivity of 0·01N-hydrochloric acid at the pressure shown, and $\Lambda_{atm.}$ the corresponding value at atmospheric pressure.

With increase in pressure the conductivity is seen to pass through a maximum value; increase in temperature decreases the influence of pressure, and also shifts the position of maximum conductivity towards lower pressure. Calculations using the Debye-Hückel formula suggest that these high pressures must cause a large change in the diameter of the ions, and that the conductivity maxima cannot be due entirely to change in degree of dissociation of the ions with pressure. These results have been applied in the study of electrolysis at high pressures.[204]

Replacement of hydrogen by deuterium in these systems results in a marked decrease in conductivity. The value of Λ_∞ for deuterium chloride in deuterium oxide is 312·6 at 25°[205] and 273·8 at 18°,[206] compared with 426·2 and

TABLE LI. - THE VARIATION IN EQUIVALENT CONDUCTIVITY OF HYDROCHLORIC ACID WITH PRESSURE

Pressure kg./cm.^{2}	$\Lambda_p/\Lambda_{atm.}$ (30°C.)	$\Lambda_p/\Lambda_{atm.}$ (75°C.)
1	1·0000	1·0000
500	1·0265	1·0125
1000	1·0464	1·0190
2000	1·0715	1·0218
3000	1·0812	1·0229
4000	1·0828	1·0225
5000	1·0780	1·0171
7000	1·0545	1·0040
9000	1·0218	0·9866
10000	1·0055	0·9780

377·5 for hydrogen chloride in water. The ionic mobility of the D^+ ion in deuterium oxide is 249·5 at 18°[205] compared with 349·9 for the H^+ ion in water, so that the difference in conductivity in the two systems arises largely from the difference in cation behaviour. When hydrogen chloride is added to deuterium oxide, or deuterium chloride to water, exchange reactions of the type $2H^+ + D_2O \rightleftharpoons 2D^+ + H_2O$ occur, so that it is not possible to obtain conductivity values which represent either of these systems ideally. However, conductivities of hydrogen chloride–deuterium chloride solutions in mixtures of water with deuterium oxide have been carried out, and typical results are given in Table LII.[207]

TABLE LII. - EQUIVALENT CONDUCTIVITY AND CATION TRANSPORT NUMBERS FOR 0·05N. SOLUTIONS OF HCl–DCl IN D_2O–H_2O MIXTURES AT 25°

Mol. fraction of D_2O	Λ	t_+
0·9853	291·68	0·8077
0·8082	301·11	0·8076
0·5990	317·46	0·8101
0·1972	366·47	0·8216
0·0002	399·08	0·8292

Similar data have been determined for 0·01N. solutions.[208,209] If Λ is plotted against the mol fraction of D_2O in the solvent, the curve obtained lies below the straight line connecting the limiting values in D_2O and H_2O. The ionic conductivity of the chloride ion varies linearly with mol fraction of deuterium oxide, so that the cation is responsible for the deviation of the conductivity values from linearity. The high mobilities of the H^+ and D^+ ions result from the symmetrical transitions:-

$$H_3O^+ + H_2O \rightleftharpoons H_2O + H_3O^+$$
$$D_3O^+ + D_2O \rightleftharpoons D_2O + D_3O^+$$

but in H_2O–D_2O mixtures the unsymmetrical transition:-

$$D_3O^+ + H_2O \rightleftharpoons D_2O + DH_2O^+$$

is also involved. This is less probable, and results in a decrease in the apparent mobility of H^+ and D^+ ions.

DIELECTRIC CONSTANT

Many measurements of the dielectric constant ϵ of hydrochloric acid have been made, mostly in very dilute solution.[210-221] Measurement of ϵ is difficult with conducting solutions, but the Fürth ellipsoid method has been used with success, though the results vary somewhat.[216–221] There is general agreement that ϵ first falls with increasing concentration, then rises to a value at least as high as that for pure water. The results given in Table LIII (which assume $\epsilon = 80$ for water) are typical.[217]

TABLE LIII. - DIELECTRIC CONSTANTS OF HYDROCHLORIC ACID

% concn.	0	0·1	0·15	0·2	0·25	0·3	0·4	0·5
ϵ	80	78·5	72·5	70·3	71·4	80·2	83·4	84·9

CATALYTIC EFFECTS

The property which hydrochloric acid possesses of catalyzing many reactions is no longer to be regarded as distinctive; the Brönsted-Lowry concept of acids and bases has served to correlate many reactions in which acids and bases have catalytic properties, and such catalysis is known to occur in many non-aqueous systems also. The general phenomenon of acid-base catalysis is considered in detail in textbooks of physical chemistry, but reference may be made here to some reactions in which catalysis by hydrochloric acid has been studied quantitatively. These reactions include the hydrolysis of hypophosphoric acid,[222] and the hydrolysis of hydrocyanic acid in acetic acid;[223] the decomposition of hydrogen peroxide;[224] the inversion of menthone;[225] the reversion of glucose and the degradation of cellulose;[226] the inversion of sucrose and the decomposition of ethyl diazoacetate;[227] the esterification of a range of aromatic acids (for which rates have been compared in the presence of hydrogen chloride and deuterium chloride),[228] and the transformation of acetylchloroaminobenzene into chloroanilides.[229]

REFRACTIVE INDEX

The refractive index of hydrochloric acid solutions, from which molar refractivities may be calculated, has been determined as a function of concentration and temperature.[230–233] Some values are given in Table LIV.[233]

TABLE LIV. - REFRACTIVE INDEX OF HYDROCHLORIC ACID

20°		30°		40°	
Normality N	Refractive Index n_D	N	n_D	N	n_D
0·0000	1·33302	0·0000	1·33251	0·0000	1·33196
0·4859	1·33708	0·4853	1·33659	0·4440	1·33566
1·2562	1·34336	1·2545	1·34283	1·2525	1·34227
2·0262	1·34950	2·0233	1·34893	2·0200	1·34833
3·0401	1·35738	3·0351	1·35675	3·0298	1·35610
4·0582	1·36514	4·0510	1·36441	4·0435	1·36374

The refractive index of water increases with fall in temperature, and since n for ice (1·31) is less than for water, there is a temperature of maximum refractivity analogous to the temperature of maximum density. This has been determined for water and some aqueous solutions by plotting the temperature coefficient of n against the temperature; extrapolation to zero coefficient then gives the temperature of maximum refraction. For water this temperature is −0·5°; for 0·5N- and 0·25N-hydrochloric acid solutions it is −4·2° and −2·1° respectively.[232]

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THE CHEMICAL PROPERTIES OF HYDROGEN CHLORIDE AND HYDROCHLORIC ACID

REACTION WITH OXIDIZING AGENTS

Hydrogen chloride and oxygen in the gaseous state react over a range of conditions to liberate chlorine according to the equation $4HCl + O_2 \rightleftharpoons 2Cl_2 + 2H_2O$. For this reaction, the relation between the equilibrium constant and temperature is given[1] by $\log K_p = 5500/T - 4{\cdot}31 \log T + 0{\cdot}00015T + 5{\cdot}18$ and other relevant volumetric relations have been calculated.[2] Hydrochloric acid containing dissolved oxygen is oxidized to chlorine when irradiated with light of wave-length 254–365 mμ and a condition of true equilibrium is reached at the stationary state. The concentration of chlorine produced increases with increasing acid concentration, but is limited by the establishment of the stationary state. The quantum efficiency of the reaction in aqueous solution at 260 mμ is 0·2, decreasing rapidly with increasing wavelength. Gaseous hydrogen chloride is only very slowly oxidized by oxygen in the light from a quartz-mercury lamp, but oxidation is almost complete in sunlight. The reaction is retarded by the removal of water vapour, and accelerated by the presence of chlorine.[3] With atomic oxygen, produced at 1 mm. pressure, hydrogen chloride reacts to the extent of 25% only, giving chlorine and water vapour, whereas under the same conditions the oxidation of hydrogen bromide is complete.[4,5] Anodic oxidation of hydrochloric acid, using a lead anode, yields perchloric acid, and has been applied to commercial production of this acid.[6] The oxidation of hydrochloric acid by excess of potassium permanganate is represented by the reaction:-

$$2KMnO_4 + 8HCl \rightarrow 2KCl + 2MnO_2 + 4H_2O + 3Cl_2;$$

the second stage:-

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$$

depends upon the presence of excess acid and application of heat.[7] These reactions are of obvious significance in volumetric analysis. Kinetic studies of the accelerated decomposition of hydrogen peroxide into water and oxygen in the presence of dilute hydrochloric acid indicate that the acid is oxidized; the rate of catalytic decomposition is determined by two compensating irreversible reactions:-[8-10]

$$H^+ + Cl^- + H_2O_2 \rightarrow HClO + H_2O$$
$$\text{and} \quad HClO + H_2O_2 \rightarrow H^+ + Cl^- + H_2O + \tfrac{1}{2}O_2.$$

Concentrated hydrochloric acid is oxidized by hydrogen peroxide to chlorine; the overall reaction is $H_2O_2 + 2HCl \rightarrow 2H_2O + Cl_2$. The rate at which chlorine is liberated is proportional to the hydrogen peroxide concentration, and is increased by the presence of other added substances such as sulphuric acid or metal chlorides. With added bivalent and trivalent chlorides the rate of chlorine liberation is almost twice that observed with univalent salts.[11]

REACTION WITH HYDROHALOGEN ACIDS AND HYDROCYANIC ACID

Anhydrous hydrogen chloride combines with hydrogen bromide at −100° to give a solid product, HCl,HBr. The existence of this compound has been demonstrated at temperatures as high as −75°.[12] Ionic structures proposed for the compound are $H_2Cl^+Br^-$ (I) and $H_2Br^+Cl^-$ (II). The cations in I and II are isoelectronic with K^+ and Rb^+ respectively, and comparison of the energy of formation of the compound HCl,HBr with that of potassium chloride and rubidium chloride supports the formulation (I) for the compound.[13] Passing hydrogen chloride into liquid hydrogen fluoride does not alter the electrical conductivity of the latter, so that no interaction occurs.[14] Measurements of the solubility of iodine in hydrochloric acid solutions have been made at various concentrations and temperatures;[15] the equilibrium constants for the reaction HCl + I_2 (dissolved) $\rightleftharpoons$ HCl,I_2 are 1·24, 1·30 and 1·38 at 25°, 35° and 45° respectively. The nature of solutions of iodine monochloride in hydrochloric acid has been investigated by studying the distribution coefficients of iodine between ICl - HCl - KCl solutions and carbon tetrachloride.[16] The ionic species present in these solutions are discussed fully elsewhere (see page 487).

Hydrogen chloride and hydrogen cyanide form addition products in various molecular proportions.[17,18] The compound HCN,HCl (NH:CHCl) is probably the intial reaction product, but it readily decomposes into its components. A small quantity only of insoluble aldimine hydrochloride is obtained when *m*-cresol is added to a dilute ethereal solution of hydrogen chloride and hydrogen cyanide. Direct reaction gives the compound HCN,2HCl ($H_2N.CHCl_2$, dichloromethylamine), the presence of which was deduced from the hydrolysis products of its nitrobenzaldehyde condensation product. The final product of direct reaction is crystalline 2HCN,3HCl (dichloromethyl) aminochloromethylamine, $H_2N.CHCl.NH.CHCl_2$. This compound when heated on a steam bath gives a glass-like product 2HCN,HCl (chloromethylene-formamide) which is of use in the preparation of derivatives of aldehydes. However, these compounds are not formed with sufficient readiness to prevent the use of liquid hydrocyanic acid as a reaction medium for reactions involving hydrogen chloride. Thus both triethylamine and pyridine in solution in liquid hydrocyanic acid absorb hydrogen chloride gas to give 99% of the calculated yield of triethylammonium and pyridinium chlorides.[19] The action of dry gaseous hydrogen chloride on liquid cyanamide affords an addition compound, $H_2NCN.HCl$.[20]

The reaction between hydrogen chloride and sodium or potassium bromide at elevated temperatures reaches an equilibrium, the position of which is temperature-dependent. The equilibrium constants and heats of reaction are as follows:-[21,22]

	$K = \frac{N_{MBr}\cdot pHCl}{N_{MCl}\cdot pHBr}$	Heat of reaction (g.-cal.)
NaCl + HBr $\rightleftharpoons$ NaBr + HCl	4·69 at 850° 4·14 at 950°	-3,400
KCl + HBr $\rightleftharpoons$ KBr + HCl	8·33 at 750° 6·10 at 850°	-8,500

REACTION WITH NON-METAL AND METAL CHLORIDES

Hydrogen chloride forms addition compounds with some non-metal chlorides and with many metal chlorides. These compounds vary widely in stability, and the behaviour in aqueous solution is frequently different from that of the anhydrous reactants. Boron trichloride forms a simple eutectic system with hydrogen chloride, and thermal analysis gives no evidence for compound formation under these conditions.[23] Freezing point-composition data show a simple eutectic system (eutectic temperature -134°) with boron trifluoride also, so that (in contrast to the fluoride ion) the chloride ion does not act as a donor to boron trifluoride.[24] The existence of the compound $BF_3,3HCl$, believed formerly to be produced as a distillation fraction from BF_3-HCl mixtures,[25] appears unlikely. Nitrogen trichloride in carbon tetrachloride solution reacts with anhydrous hydrogen chloride according to the equation:-

$$4HCl\ (gas) + NCl_3\ (in\ CCl_4) \rightarrow NH_4Cl\ (solid) + 3Cl_2\ (gas).$$

The heat of reaction is 41·80 kg.-cal., and the heat of solution of hydrogen chloride in carbon tetrachloride is 3·68 kg.-cal.[26] The absorption of hydrogen chloride by silicon tetrachloride has been studied tensimetrically over the temperature range -50° to -80°. Only at -80° was there evidence of combination, when up to 3 mols. of hydrogen chloride were absorbed per mol. of silicon tetrachloride. No evidence was obtained for the direct formation of hexachlorosilicic acid.[27] The phase diagram for sulphur monochloride with hydrogen chloride shows two eutectics; for 26 mol.-% HCl at -119° and for 98 mol.-% HCl at -112°. The liquid mixture separates into two layers, and pale yellow crystals of composition $H_4S_2Cl_6$ separate from the upper layer at -92·5°.[28] Isotope exchange reactions using hydrogen chloride containing ${}^{35}Cl$ atoms show that exchange of chlorine occurs rapidly with arsenic trichloride and phosphorus trichloride, but more slowly with phosphorus oxychloride. Exchange is very slow with silicon tetrachloride and sulphur monochloride, and does not occur at all with carbon tetrachloride.[29]

The well-known 'salting out' of metal chlorides from aqueous solution by hydrogen chloride has received much attention. This common ion effect (which is related also to the hydration of the ions present) is pronounced with sodium and potassium chlorides, and may be employed in their purification. The change in solubility with hydrochloric acid concentration is illustrated in Table LV.[30]

TABLE LV.- SOLUBILITY OF SODIUM AND POTASSIUM CHLORIDES IN AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID AT 25°

(concns. in g.-mols./1000 c.c. saturated solution)

Concn. HCl	Solubility of NaCl	Concn. HCl	Solubility of KCl
0·0	5·433	0·0	4·199
0·886	4·483	1·492	2·887
3·487	2·079	3·570	1·449
5·253	0·907	5·672	0·607
7·073	0·293	7·144	0·309
9·236	0·091	10·68	0·215
13·41	0·017	12·96	0·24

Viscosities and densities of these solutions have also been determined,[30,31] and the KCl-HCl-H_2O system has been studied over the temperature range 25° to 80°C.[32] Although hydrogen chloride lowers the solubility of potassium chloride, it does not alter the general form of the solubility-temperature curves. Hydrogen chloride lowers the solubility of sodium chloride to a greater extent than does sodium hydroxide.[33] The phase systems $AlCl_3$-HCl-H_2O and $AlCl_3$-KCl-HCl-H_2O have been determined, but no addition compounds or mixed crystals were observed.[34,35] The system $BeCl_2$-HCl-H_2O has been examined by hydrolysis of beryllium chloride and by using solutions of the phases $BeCl_2,2H_2O$ and $BeCl_2,4H_2O$ in aqueous hydrochloric acid. Solutions in which the ratio BeO:HCl is 1:2 may be obtained if a slow stream of gaseous hydrogen chloride is passed into a saturated solution of beryllium chloride.[36] Magnesium, strontium and barium chlorides can be almost completely salted out of solution by means of hydrogen chloride, but for a similar effect cadmium, zinc and calcium chlorides in solution must be saturated with hydrogen chloride under increased pressure. In the $CdCl_2$-HCl-H_2O system from an HCl concn. up to 6%, the solid phase is $CdCl_2,2{\cdot}5H_2O$, from 6-11% it is $CdCl_2,H_2O$, from 11-22% it is $2CdCl_2,HCl,4H_2O$ and from 22-27% it is $CdCl_2,HCl,3H_2O$.[37] Similarly, $2ZnCl_2,HCl,H_2O$ and $2ZnCl_2,HCl,2H_2O$ may be precipitated from zinc chloride solutions by means of hydrogen chloride.[38] Precipitation of $AlCl_3,6H_2O$ from ether-water mixtures occurs on saturating the mixture at 0° with hydrogen chloride. This fact also affords a convenient method for the separation of aluminium from Be, Ca, Mn, Co, Zn, SO_4 and PO_4 ions, and in view of the possible application of this device in analytical chemistry, solubilities have been determined for a series of metal chlorides at 0° in a solution made by saturating with hydrogen chloride a mixture of equal volumes of ether and water.[39]

Treatment of hydrated ferric chloride with hydrogen chloride produced a range of hydrated chloro acids, in which the $FeCl_3$:HCl:H_2O ratio may be 1-1-2, 1-1-4, 1-1·5-4·5, 1-2-5·5, 1-2·5-6 and 1-3-7.[27] The compounds vary widely in colour and physical properties, and are clearly co-ordination complexes which may contain chloro-, aquo- or hydroxy-groups. Some of these complexes, and the influence of hydrochloric acid concentration on their composition, have been investigated by measuring the distribution of ferric chloride between aqueous acid solutions and ether.[40] The formation of complex ions (ultimately of the form $[MCl_6]^{3-}$ in sufficiently high concentrations of hydrochloric acid) has been shown for solutions of the trichlorides of aluminium, gallium, indium, lanthanum and iron in hydrochloric acid by measuring their heats of solution. This decreases markedly (and to about the same extent) as the hydrochloric acid concentration is increased. It has been suggested that the formation of such complex ions is an endothermic reaction, resulting from the strong binding between the chlorine ion and the water molecule.[41] The addition of hydrochloric acid to a pink aqueous solution of cobaltous chloride changes the colour to blue, and the changes occurring in the solution have been followed by measurements of viscosity,[42] magnetic properties,[43] and electrical conductivity,[44,45] and by absorption spectroscopy.[46] At high acid concentration the ion $[CoCl_4]^{2-}$ is predominant, whereas at low acid concentrations the metal ion is in the form of the 6-co-ordinate aquo complex $[Co(H_2O)_6]^{2+}$. As a result of the strong electron donor properties of the chloride ion, many co-ordination complexes undergo change when dissolved in hydrochloric acid: for example, the hexamminochromic complex ion is converted to the chloropentammino-chromic ion in hydrochloric acid.[47] A large number of such examples is known but they will be mentioned under the appropriate elements and need not be discussed here.

The solubility of nickel, cobalt and cupric chlorides in water shows an initial rapid decrease on addition of hydrochloric acid, owing to the common ion effect; the solids in equilibrium with these solutions are the simple salt hydrates. There is a subsequent increase in solubility of these salts at higher acid concentration, owing in each case to complex ion formation, but the increase is most marked with cupric chloride, and from this solution a compound HCl,$CuCl_2$,$3H_2O$ may be isolated at 0°.[48] The change in electrical conductivity on adding hydrochloric acid to cupric chloride solutions indicates[49] the formation of the ions $[CuCl_3]^-$ and $[CuCl_4]^{2-}$. Spectrophotometric and refractometric measurements confirm the existence of these ions in the solutions, and the former ion is probably hydrated as $[Cu(H_2O)Cl_3]^-$ to preserve the 4-co-ordination of copper.[50,51] The species $CuCl^+$ (or $[Cu(H_2O)Cl]^+$) and $Cu(H_2O)_2Cl_2$ may also be present.[50,52] More complicated systems such as $CuCl_2$ - NH_4Cl - HCl - H_2O have also been investigated.[53] The vapour pressure of hydrochloric acid solutions decreases linearly with increase in the concentration of added cuprous chloride, whereas the vapour pressure increases on adding lithium chloride;[54] this is consistent with the formation of $[CuCl_2]^-$ ions in solution, the existence of which is supported also by measurements of the solubility of cuprous chloride in hydrochloric acid.[55] Potential measurements have also served to elucidate the nature of solutions of chlorides in hydrochloric acid. Oxidation–reduction potentials of thallous–thallic salts in hydrochloric acid are interpreted in terms of chlorothallate ions of the type $[TlCl_4]^-$ and $[TlCl_6]^{3-}$; most of the thallic ions are in the form of such complexes, there being an average of 3·5 chlorine atoms per complex in the hydrochloric acid concentration range 0·1 – 1 N.[56] Hydrochloric acid reacts with antimony chlorides in aqueous solution, and the formal potential of the antimonous–antimonic half-cell has been interpreted[57] in terms of equilibria involving the ions $[SbCl_4]^-$, $[SbCl_6]^-$, $[Sb(OH)_xCl_y]^-$ and $[Sb_2Cl_{10}]^{2-}$. The wide variation in the stability of complexes of hydrogen chloride with metal chlorides may be used in their separation; for example, the compounds $AsCl_3$, $SbCl_3$, $SnCl_4$ and $TiCl_4$ may be removed completely from germanium tetrachloride by extracting the latter with concentrated hydrochloric acid.[58]

Although in aqueous solution hydrochloric acid forms addition compounds with many metal chlorides, examples of the formation of addition compounds with anhydrous metal chlorides are few, though combination occurs more readily with the salt hydrates. Titanium tetrachloride does not absorb hydrogen chloride from the gaseous phase at −50° or at −65°[27] but the thermal diagram of the system $HCl - TiCl_4$ shows the existence of two compounds $TiCl_4,6HCl$ (m.p. −86°) and $TiCl_4,2HCl$ (m.p. −30·8°); each compound melts congruently.[59] Anhydrous stannic chloride does not absorb hydrogen chloride, but reaction with the pentahydrate gives the acids $5H_2SnCl_6,6H_2O$ and $3H_2SnCl_6,6H_2O$.[27] The thermal diagram for the system $HCl - SnCl_4$ shows two compounds $SnCl_4,5HCl$ and $SnCl_4,2HCl$, having congruent melting points of −94·7° and −85·4° respectively.[60] Alkyl- or aryl-chloro compounds of tin may be prepared by bubbling hydrogen chloride into the liquid organo-metallic compounds; Me_2Et_2Sn gives $MeEtSnCl_2$, Et_2Pr_2Sn gives $EtPrSnCl_2$, but Ph_2Et_2Sn gives Et_2SnCl_2.[61]

REACTION WITH OTHER BINARY COMPOUNDS

Gaseous hydrogen chloride reacts quantitatively with the nitrides of aluminium, magnesium, calcium, titanium and boron, forming the chloride and ammonia, at temperatures in the range 650° to 1050°.[62] At 750°, hydrogen chloride gas reacts with vanadium carbide forming methane, hydrogen and the chlorides VCl_2 and VCl_3.[63] Vanadium carbide is insoluble in aqueous hydrochloric acid, and is unchanged by it. The reaction of hydrogen chloride (both in the gaseous and pure liquid state) with calcium carbide is slow, since a coating of solid reaction products protects the carbide from further attack.[64] The extent to which hydrochloric acid reacts with metal sulphides determines the conditions under which these sulphides are precipitated from aqueous solutions of metal salts using hydrogen sulphide. Because of the significance of these reactions in qualitative analysis, the critical hydrochloric acid concentration for separation of a range of metals as sulphides has been determined.[65,66] For example,[67] in the reaction $CdS + HCl \rightleftharpoons H_2S + CdCl_2$:-

$$K = \frac{[CdCl_2][H_2S]}{[HCl]^2} = 1{\cdot}06 \times 10^{-6}.$$

Black mercuric sulphide is attacked by hot or cold 5 – 20% hydrochloric acid, but the red sulphide is unchanged in the cold acid.[68] At high temperatures, gaseous hydrogen chloride will react with dry metal sulphides. For the zinc sulphide–hydrogen chloride system, log K_p is 1·14 at 565°K. and 1·67 at 635°K.[69] The manganese sulphide reaction has also been studied quantitatively over the temperature range 680 – 1000°K.[69] When equilibrium is established between anhydrous cadmium chloride and hydrogen sulphide, 76·5% of the available quantity of hydrogen chloride is liberated at 352°, and 13·1% at 232°. The extent of conversion to sulphide is less in the case of manganese and silver chlorides.[70] In liquid hydrogen sulphide, hydrogen chloride shows acidic properties and will react with the base sodium hydrosulphide to give sodium chloride.[71] The reaction $HCl + NaSH \rightarrow NaCl + H_2S$ may be regarded as an acid-base reaction if liquid hydrogen sulphide is considered as a solvent system analogous to water. The reaction:-

$$Et_3NH.HS + HCl \rightarrow Et_3NHCl + H_2S$$

may be followed by conductometric titration in liquid hydrogen sulphide.[71]

Hydrochloric acid reacts readily with metal borides. The reaction between magnesium boride and hydrochloric acid to give hydrogen and boron hydrides is well known, and the special experimental techniques employed for separation of the reaction products have been fully described.[72] The silicon hydrides may be prepared similarly from magnesium silicide and 20% hydrochloric acid. The intermediate compound $H_2Si[Mg(OH)]_2$ is first formed in this reaction; this then reacts with hydrochloric acid thus:-

$$H_2Si[Mg(OH)]_2 + 4HCl \rightarrow 2MgCl_2 + 2H_2O + H_2 + SiH_2$$

and a series of silicon hydrides is obtained by polymerization of the SiH_2 radical.[73] An amorphous solid of empirical composition SiH_2 is formed by the action of a saturated solution of hydrogen chloride in absolute alcohol on calcium monosilicide.[74] Mono- and dichloro-silanes are prepared by the action of hydrogen chloride on monosilane at 100°, with aluminium chloride as catalyst.

$$SiH_4 + HCl \rightarrow SiH_3Cl + H_2; \quad SiH_3Cl + HCl \rightarrow SiH_2Cl_2 + H_2$$

Hydrogen chloride reacts with powdered silicon at 350° giving silicochloroform ($SiHCl_3$) and silicon tetrachloride.[75] The action of dilute hydrochloric acid on magnesium germanide gives a mixture of the germanium hydrides, and with calcium germanide (CaGe) the polymerized hydride $(GeH_2)_x$ is produced.[76] Reactions may also be autocatalyzed by small quantities of hydrogen chloride. Thus the reaction between chlorine and a mixture of silicon with magnesium oxide to give silicon tetrachloride begins at 400 – 500°, with yields not exceeding 30%, but when the chlorine carries a trace of hydrogen chloride the reaction begins at 300°, and yields are higher.[77] In the preparation of carbides of molybdenum, tungsten and titanium by the reaction of carbon with the free metal or its oxide, the presence of small amounts of hydrogen chloride accelerates the rate of reaction; the $TiO_2 - C$ reaction is particularly sensitive.[78]

REACTION WITH OXIDES AND HYDROXIDES

Reaction between hydrochloric acid and aqueous solutions of strong alkalies is a simple ionic reaction which usually gives the normal salt directly. The heat of reaction of beryllium hydroxide with hydrochloric acid is 13·65 kg.-cal., close to the value for neutralization of strong bases with strong acids.[79] When gaseous hydrogen chloride is absorbed in aqueous alkaline solutions the surface processes involved are complex, since the absorption rate in alkali (with or without the presence of surface active substances) is less than in pure water.[80] In the course of solubility product determinations, the equilibria in the simple systems $Ni(OH)_2 - HCl$,[81] $Mn(OH)_2 - HCl$[82] and $SnO - HCl$[83] have also been studied. With weak bases the neutralization reaction frequently proceeds in several stages, involving the intermediate formation of basic salts. Although aluminium chloride is the final product of reaction betweem aluminium or its oxide with excess of concentrated hydrochloric acid, the solution of aluminium in dilute acid at 80° in the molar ratio 1:1 gives the basic chloride $Al(OH)_2Cl$.[84] Studies of the rate of solution of oxides is complicated by colloidal phenomena. The initial rapid rate of neutralization of hydrochloric acid by hydrated alumina is attributed to the instantaneous neutralization of the hydroxy-groups on the surface of the alumina particles; the subsequent slower neutralization is explained in terms of the solid structure of the oxide, but the rate of the diffusion process in the neighbourhood of the solid surface must be significant also.[85] The reaction between colloidal ferric hydroxide and hydrochloric acid is also a complicated one; addition of acid first causes peptization, and during this stage the charge on the ferric hydroxide particles passes through a maximum (compare silica sols).[86] The adsorption of ions on the particle then causes coagulation. The rate of reaction is increased by increase in temperature and acid concentration, and is considerably influenced by the degree of dispersion of the precipitate, which in turn depends upon the ferric chloride concentration in solution, and the age of the solution. Several quantitative studies of the system have been made.[87-89] The difference in particle size of precipitate also explains the difference in reaction rate of hydrochloric acid with α- and β-stannic oxides; coalescence of primary particles is greater with the β-oxide, and the rate of reaction is slower.[90] The temperature of precipitation of titanium dioxide has a considerable effect on its solubility in acid. When the dioxide was prepared at 25°, none was found in the colloidal state at acid concentrations exceeding 0·25 N., whereas with dioxide prepared at 100° the colloidal condition persisted at acid concentrations up to 1·5 N.[91] The solubility curve for mercuric oxide in hydrochloric acid shows a break owing to the formation of the solid phase $HgCl_2,2HgO$[92] and the compound $Pb(OH)Cl$ may be readily obtained from lead acetate with hydrochloric acid.[93] Hydrated antimonous oxide reacts with hydrochloric acid to give a range of oxychlorides, the composition of which is determined by the concentration of reactants. Compounds of empirical formulae $Sb_4O_3(OH)_5Cl$, $Sb_4O_3(OH)_3Cl_3$, $SbOCl$ and $Sb_4O_5Cl_2$ have been reported; some are metastable.[94] The ternary system bismuth oxide–hydrochloric acid–water has been studied, and bismuth oxychloride is found to be the only stable phase separating up to the point represented by 33·7% HCl, 50·7% Bi_2O_3, 7·6% H_2O.[95] Oxychlorides are also produced by reaction of hydrogen chloride at elevated temperatures with metal oxides. Niobium pentoxide reacts slowly at 400°, and rapidly at 700°, with hydrogen chloride according to the equation:-

$$Nb_2O_5 + 6HCl \rightleftharpoons 2NbOCl_3 + 3H_2O.$$

The equilibrium constant is about 10^{-16} at 600°. The position of equilibrium, and thus the degree of hydrolysis of the compound $NbOCl_3$, varies with temperature; on cooling, the reaction products separate in the following order; Nb_2O_5 at 600°–400°, NbO_2Cl at 300°, and below 300° a mixture of the compounds Nb_2O_5, $NbOCl_3$, NbO_2Cl, HCl and H_2O.[96] Reaction with tungstic oxide commences at 300°, and is complete after six hours at 400°, giving the yellow oxychloride WO_2Cl_2. With sodium tungstate, the reaction proceeds in two stages:-

$$Na_2WO_4 + 2HCl \rightarrow 2NaCl + WO_3 + H_2O$$
$$\text{followed by} \quad WO_3 + 2HCl \rightarrow WO_2Cl_2 + H_2O,$$

the most favourable temperature being 500°. The sodium polytungstates also react, the reaction rate increasing with increase in WO_3 content. Metallic tungsten does not react, even at 600°, with hydrogen chloride, but both oxides WO_2 and W_2O_5 react at 400° to give the compound WO_2Cl_2, leaving a residue of metallic tungsten.[97] The equilibrium between hydrogen chloride and α-ferric oxide has been investigated over the temperature range 300–1000°C.[98] The equilibria concerned are:-

$$(1)\quad Fe_2O_3(s) + 6HCl(g) \rightleftharpoons 2FeCl_3(g) + 3H_2O(g)$$
$$(2)\quad Fe_2O_3(s) + 6HCl(g) \rightleftharpoons Fe_2Cl_6(g) + 3H_2O(g)$$
$$(3)\quad 2FeCl_3(g) \rightleftharpoons Fe_2Cl_6(g)$$

The variation in the equilibrium constants with temperature is given by:-

$$\log K_{(1)} = -2{\cdot}935 - (29{\cdot}3 \times 10^3/4{\cdot}57\ T)$$
$$\log K_{(2)} = -11{,}853 + 340/4{\cdot}57\ T$$
$$\log K_{(3)} = -9{,}800 + (32{\cdot}55 \times 10^3/4{\cdot}57\ T)$$

The vapour density of ferric chloride at 450° corresponds with the dimer Fe_2Cl_6, but dissociation to $FeCl_3$ is practically complete at 750°; $K_{(1)}$ is therefore important above 450°, whereas $K_{(2)}$ is important below this temperature. The presence of small amounts of hydrogen chloride increases the rate of reduction of ferric oxide by hydrogen at 300°–600°.[99] Interesting reactions occur between hydrogen chloride and the tetroxides of ruthenium and osmium. With ruthenium tetroxide, tetrachlororuthenic acid is produced by the reaction:-[100]

$$RuO_4 + 6HCl\ (gas) \rightarrow H_2[RuO_2Cl_4] + Cl_2 + 2H_2O$$

and the same compound is obtained during the decomposition of ruthenium tetroxide by aqueous hydrochloric acid. On further treatment with concentrated hydrochloric acid, the reaction:-

$$H_2[RuO_2Cl_4] + 4HCl \rightarrow H_2[RuCl_6] + Cl_2 + 2H_2O$$

occurs, and the trichloride $RuCl_3$ may also be isolated from the reaction products.[101] The reducing properties of hydrogen chloride have often been utilized in the study of the chemistry of elements of variable valency; if potassium chlororuthenate ($K_2[RuCl_6]$) is heated at 540° in a stream of hydrogen chloride gas, it is reduced to the chlororuthenite K_2RuCl_5.[100] Hydrochloric acid converts osmium dioxide into osmium tetrachloride, which probably exists in hydrochloric acid solution as the acid $H_2[OsCl_6]$;[102] the reaction:-

$$OsO_2 + 6HCl \rightleftharpoons H_2[OsCl_6] + 2H_2O$$

is reversible. If the vapour of osmium tetroxide is passed into dilute hydrochloric acid no reaction occurs, but if the density of the acid exceeds 1·16 the tetroxide is converted to the tetrachloride;[101] intermediate compounds are formed and the deliquescent brown crystals which have been separated from the solution probably have the oxychloride constitution $Os(OH)Cl_3$.[103] This compound is no doubt present in hydrochloric acid solution as $H_2[Os(OH)Cl_5]$. Titanium dioxide reacts with hydrogen chloride over a wide temperature range; the reaction has been studied with hydrogen chloride gas at 200°, and with pure liquid hydrogen chloride at low temperatures: in each case the yellow 2:1 compound $Ti(OH)_2Cl_2$ is formed.[104] In the presence of water a trihydrate is produced. Uranium trioxide reacts similarly, forming the uranyl compound $UO_2(OH)Cl$, which gives a dihydrate in the presence of water.[104]

REACTION WITH NON-METALS AND NON-METAL OXIDES

Compound formation between hydrogen chloride and the inert gases has been postulated. The ability of the inert gases to form compounds has long been a matter of doubt; however, in the presence of a strong dipole the atom may become sufficiently polarized to form addition complexes by dipole-dipole attraction. At sufficiently low temperatures and pressures, crystals of hydrogen chloride take up appreciable quantities of radon, which may be separated from argon and neon by this means.[105] The second virial coefficient for krypton–hydrogen chloride mixtures has been studied as a function of composition, and the results suggest that there is some association between the components.[106,107] Experimental study of the $P-V-T$ relations for gaseous mixtures of propane with hydrogen chloride leads to similar conclusions.[107] During a study of the rate of reaction of hydrogen chloride with atomic hydrogen, it was observed that much heat was liberated in that part of the apparatus where the hydrogen atoms (produced by electric discharge) came into contact with hydrogen chloride, and that the presence of hydrogen chloride promoted rapid recombination of hydrogen atoms. This is due to the initial reaction $H + HCl \rightarrow Cl + H_2$, followed by a rapid reaction $H + Cl \rightarrow HCl$, which thus regenerates the hydrogen chloride.[108] Numerous reactions involving non-metal oxides have also been clarified. Early reports that a contraction in volume occurs when carbon monoxide and hydrogen chloride gases are subject to electric discharge, due to the reaction $CO + HCl \rightarrow HCOCl$, have been re-examined.[109] Sparks were passed between nickel and molybdenum electrodes in equimolar mixtures of the dry gases, but for times of contact up to 50 hours, pressures up to 250 kg./sq.cm. and temperatures up to 250°, no evidence of reaction was observed. The existence of the addition compound is usually postulated to explain the reaction of a CO-HCl gas mixture with aromatic hydrocarbons, which forms an aldehyde in the presence of aluminium halide as catalyst: $RH + HCOCl \rightarrow RCHO + HCl$ (Gattermann-Koch reaction). However, the reaction kinetics of the process indicate the formation of ions by the reaction $HCl + CO + AlBr_3 \rightarrow AlBr_3Cl^- + HCO^+$, followed by the rate-determining reaction $HCO^+ + RH \rightarrow R.CHO + H^+$.[110] When nitric oxide and hydrogen chloride are condensed together at 120-130°K., a blue liquid containing the addition compound NO,HCl is obtained.[111] It has been claimed that this compound is not formed in the absence of traces of nitrogen dioxide or oxygen.[112] The liquid has an electrical conductivity greater than 10^{-3} ohm^{-1}, and the compound may be formulated as the ionic form NOH^+Cl^-. Hydrogen chloride reacts rapidly with nitrogen dioxide in the dark:-

$$2HCl + NO_2 \rightarrow NOCl + H_2O + \tfrac{1}{2}Cl_2$$

and no nitric oxide is found in the products.[113] In an experiment in which the gases were mixed at partial pressures of 3·5 mm. (NO_2) and 8·3 mm. (HCl), 50% of the nitrogen dioxide (measured photometrically) reacted almost immediately, and 85% within ten minutes. It has been claimed that dry hydrogen chloride is absorbed by phosphoric oxide, the absorption curve being autocatalytic in type.[114] The initial period of delay was increased to as much as seven days by intensive drying of the hydrogen chloride over phosphoric oxide prior to the experiment, and the subsequent increase in absorption rate was attributed to the catalytic effect of the intermediate compounds PO_2Cl and $P_2O_3Cl_4$. However, it seems probable that in the complete absence of moisture in either reactant, no reaction whatsoever occurs.[115] The presence of traces of moisture or metaphosphoric acid has been found to give rise to a reaction which is autocatalytic. This may be explained by the reversible reaction:-

$$HCl + HPO_3 \rightleftharpoons POCl_3 + 2H_2O.$$

In the presence of large amounts of phosphoric oxide, the reaction will proceed slowly to the right, one molecule of metaphosphoric acid giving two molecules of water, which then give four molecules of metaphosphoric acid. As the amount of acid increases, so does the absorption of hydrogen chloride. If fairly pure phosphoric oxide is used as a drying agent for hydrogen chloride, no serious contamination of the gas is likely to occur in the early stages, but phosphoric oxide is not an ideal drying agent unless followed by condensation and fractionation of the hydrogen chloride.

Selenium dioxide and hydrogen chloride form two addition compounds.[116,117] The compound $SeO_2,4HCl$ is a yellow solid stable at 0°, and the compound $SeO_2,2HCl$ is a yellow liquid which is stable up to 170°. The latter compound may be prepared also from selenium oxychloride by direct reaction with an equimolar quantity of water. At 20°, its density is 2·252 and the surface tension 51·6 dynes/cm. Tellurium dioxide also absorbs hydrogen chloride at 0°, presumably to give compounds similar to those of selenium, but they are of low stability, and the product loses water continually with increasing temperature. No evidence for formation of a definite compound was found in the temperature range 0 - 150°.[116] Selenium is practically insoluble in pure concentrated hydrochloric acid, but is quite soluble in acid containing selenium dioxide. In these solutions the chloride Se_2Cl_2 is formed, which is regarded as responsible for the intense yellow colour always observed.[118,119]

REACTION WITH OXY-ACIDS AND THEIR SALTS

Hydrochloric acid reacts with the oxyacids and their salts in a variety of ways. The kinetics of the oxidation of hydrochloric acid in aqueous solution by oxyhalogen acids HXO_3 give a rate equation:-

$$\frac{-d(XO_3^-)}{dt} = -kF(XO_3^-)^x(Cl^-)^y(H^+)^z$$

where F is the activity factor and x, y and z represent the order of reaction with respect to each component.[120] With different hydrohalogen acids, the velocity of reduction of a given acid HXO_3 is in the order HI > HBr > HCl, and the ease of oxidation of HCl by oxyhalogen acids follows the order HIO_3 > $HBrO_3$ > $HClO_3$. The orders of reaction x, y and z for hydrochloric acid reactions are:-

	x	y	z
$HClO_3$ - HCl	1	1	2
$HBrO_3$ - HCl	1	2	2
HIO_3 - HCl	1	4	4

and the following rate-determining mechanisms have been postulated:-

$$HClO_3 + HCl \rightarrow HClO_2 + HClO$$
$$BrO_3^- + 2HCl \rightarrow BrO^- + 2HClO$$
$$IO_3^- + 4HCl \rightarrow IO^- + 2Cl_2 + 2H_2O.$$

A mixture of one volume of nitric acid with three to four volumes of hydrochloric acid is well known as aqua regia; the formation of nitrosyl chloride is usually represented thus:- $HNO_3 + 3HCl \rightarrow NOCl + Cl_2 + 2H_2O$. The reaction of nitric acid in a large excess of hydrochloric acid has been studied in aqueous solution at 60°, when the same equation is found to hold. The reaction is unimolecular with respect to nitric acid, with a temperature coefficient of 2·54. Silver sulphate catalyzes the reaction, but the addition of chlorides appears to have no effect.[121] Studies on the phase and reaction equilibria in the systems HNO_3 - HCl,[122] HNO_3 - HCl - H_2O,[122] and HCl - HNO_3 - HNO_2[123] have also been made. Direct reaction with sulphur trioxide, HCl + $SO_3 \rightarrow SO_2(OH)Cl$, gives liquid chlorosulphonic acid, which may also be prepared by passing dry hydrogen chloride gas into fuming sulphuric acid and then distilling. Chlorosulphonic acid, in admixture with excess sulphur trioxide, found wartime use at sea as a smoke generator owing to its ready hydrolysis in moist air. It is an important compound in the system H_2O - HCl - SO_3, which has been studied by thermal and ebullioscopic methods. In this system two compounds, $H_2S_2O_7, SO_2(OH)Cl$, m.p. 2·6°, and $H_2S_2O_7, 2SO_2(OH)Cl$, m.p. 3·1°, have been identified.[124] The addition of dilute hydrochloric acid to sodium thiosulphate gives an immediate precipitation of sulphur; 80 - 90% of the salt decomposes according to the equation $Na_2S_2O_3 + 2HCl \rightarrow SO_2 + S + 2NaCl + H_2O$, but some polythionic acids are also formed in solution.[125] If, however, concentrated fuming hydrochloric acid is used, a clear, colourless solution of the thiosulphate is obtained, and thiosulphuric acid, $H_2S_2O_3$, is believed to persist without decomposition for some time in this medium.[126] This stability is explained on the assumption that the dissociation equilibrium $H_2S_2O_3 \rightleftharpoons HSO_3^- + H^+$ is displaced far to the left in concentrated hydrochloric acid, and that the undissociated acid does not undergo decomposition.[127] The polythionic acids ultimately formed contain up to 14 sulphur atoms per molecule. Selenic acid is readily reduced to selenious acid by boiling with dilute hydrochloric acid: $H_2SeO_4 + 2HCl \rightarrow H_2SeO_3 + H_2O + Cl_2$, although hydrogen sulphide and even sulphur dioxide bring about this reduction only with great difficulty. It has been suggested that it is the undissociated molecules of selenic acid which undergo reduction.[128] The reaction may be used for the volumetric determination of selenic acid.[129] Hydrochloric acid reduces vanadates quickly and quantitatively to compounds containing tetravalent vanadium. The reaction may be represented by $V_2O_5 + 6HCl \rightarrow 2VOCl_3 + 2H_2O$, followed by $2VOCl_3 \rightarrow 2VOCl_2 + Cl_2$. The velocity of reduction is proportional to $[HCl]$, $[NH_4VO_3]$ and temperature, and when precipitating vanadium pentoxide from a vanadate solution the acid concentration should not exceed 5 N. at room temperature, or 2·8 N. at 100°.[130] The reduction is also catalyzed by Ag^+, Pb^{2+} and Cu^{2+} ions.[131] Molybdates and tungstates are not reduced under these conditions; excess of acid leads to precipitation of the trioxides, but various polymolybdates and polytungstates are formed by reaction with more dilute acid.[132,133] This property, however, is not specific to hydrochloric acid, and so need not be further discussed here. The readiness with which hydrofluoric acid will form addition compounds has led to a search for corresponding compounds of hydrogen chloride; the existence of the compound HCl,H_2SO_4 (formulated as $H_2Cl^+.HSO_4^-$) has been claimed, and also the perchlorate $H_2Cl^+.ClO_4^-$, although the explosive decomposition of the latter compound prevented its isolation.[134] Pure phosphoric acid absorbs 8% by weight of dry gaseous hydrogen chloride; mixtures show a decrease in pH with decrease in electrical conductivity, and the existence of the 1:1 compound H_4PO_4Cl has been suggested.[135] In connection with the treatment of calcium phosphates by hydrochloric acid a detailed physico-chemical study has been made of the system $CaO-P_2O_5-HCl-H_2O$, and of the solid phases obtained under various conditions.[136] At 25° there are five crystallization fields corresponding to the products (1) $CaHPO_4$, (2) $Ca(H_2PO_4)_2,H_2O$, (3) $Ca(H_2PO_4)_2,CaCl_2,2H_2O$ (a new double salt), (4) $CaCl_2,6H_2O$ and (5) $CaCl_2,4H_2O$. If the hydrochloric acid concentration is above 19·7% it will convert phase (2) to phase (3), but below this concentration it is unable to react with (2). At 40° phase (4) is missing.

Hydrogen chloride forms interesting addition compounds with the anhydrous sulphates of certain metals. The ability to form such complexes depends upon the electronic structure of the metal, since they are formed by sulphates of the metals Cu, Ag, Zn, Cd, Hg, Tl, Sn, Pb, Sb and Bi, but not by the sulphates of the alkali metals, the alkaline earth metals, Al, La, Ce, Mn, Fe, Co or Ni.[137] Using the long form of the periodic table it is possible to draw a clear dividing line between these two groups of metals. The complexes are quite distinct from the double salts obtained on crystallization of alkali metal sulphates in the presence of hydrochloric acid.[138,139] One molecule of sulphate takes up two molecules of hydrogen chloride, except in the case of zinc sulphate, which forms $ZnSO_4,HCl$.[140] Reaction occurs at a temperature peculiar to each salt; the sulphates of cadmium, copper and silver take up two molecules of hydrogen chloride at room temperature, whereas lead and zinc sulphates must be cooled. Mercuric sulphate absorbs little hydrogen chloride at room temperature, but absorption becomes violent at 125°. When treated with concentrated sulphuric acid, the complexes decompose at characteristic temperatures, and each compound has a characteristic temperature for thermal decomposition; the compound $HgSO_4,2HCl$ shows the greatest resistance to heat. At the temperature of first decomposition, half a molecule of hydrogen chloride is still retained but may be driven off at a higher temperature, so that other addition compounds may also exist. The compounds are probably 4-co-ordinate complexes, which in the case of divalent metals may be represented as $H_2[M.SO_4Cl_2]$; the problem of their constitution appears to merit further consideration. The use of heavy metal sulphates (especially copper sulphate) has been proposed for the purification, storage and transport of anhydrous hydrogen chloride.[141-143] This may be achieved by passing the dry gas (alone or mixed with non-reactive gases, e.g. air) through vessels containing the metal sulphate, alone or as infusorial earth impregnated with the salt. The hydrogen chloride is absorbed from the gas stream; it may be stored and transported in this form, and recovered by the application of heat to the vessel.

REACTION WITH AMMONIA: CHEMICAL FOGS

The part played by moisture in the combination of hydrogen chloride and ammonia gases, and the question whether combination occurs in the complete absence of moisture, is a subject of continued discussion.[144] When the carefully dried gases meet in a tube, Liesegang rings of ammonium chloride are formed, and moisture appears to play no significant part.[145] From osmotic studies of dilute mixtures, the existence of an addition compound $HCl,4NH_3$ has been postulated.[146] If hydrogen is completely replaced by deuterium, the corresponding reaction $ND_3 + DCl \rightarrow ND_4Cl$ takes place; the low temperature transition of the compound ND_4Cl has been compared with that of ammonium chloride.[147] The formation of ammonium chloride by gaseous reaction is considered to play an important role in the production of the fogs which are frequently encountered when hydrogen chloride is absorbed from a gas stream by bubbling through alkaline solutions; these fogs are strongly acid, and since they are difficult to absorb again, they can give rise to considerable errors in quantitative analysis. No fog is formed when air–HCl mixtures are bubbled through concentrated potassium hydroxide solutions, but with dilute sodium or potassium hydroxides a heavy fog often forms.[148] This is attributed to traces of ammonia, the first step in fog production being the formation of ammonium chloride within the gas bubbles.[149] The quantity of fog at first increases with increase in quantity of added ammonia, and then becomes constant. When a gas containing hydrogen chloride is bubbled through ammonium hydroxide solution, fogs are invariably formed.[150]

REACTION WITH DEUTERIUM

Reaction between hydrogen chloride and deuterium gives rise to a number of equilibria, amongst which are the following:-

$$1.\ D_2 + HCl \rightleftharpoons HD + DCl$$
$$2.\ H_2 + DCl \rightleftharpoons HD + HCl$$
$$3.\ H_2 + 2DCl \rightleftharpoons D_2 + 2HCl.$$

Thermal exchange above 700°K. has been studied using a quartz reaction vessel; below this temperature platinum black has been used as catalyst. The reactions require about a day to reach equilibrium, and the constants for the various equilibria have been calculated.[151,152] Reaction (1) is homogeneous and bimolecular at temperatures up to 830°K. Above this temperature, reaction can also take place by the agency of thermally dissociated atoms (a surface reaction) according to the chains $D + HCl \rightarrow HD + Cl$, and $Cl + D_2 \rightarrow D + DCl$; the reaction $D + HCl \rightarrow DCl + H$ does not occur.[153,154] The equilibrium constants for reaction (3) differ appreciably from unity;[155,156]

and the heat of reaction is -1100 g.-cal./mol.[156] Reaction (1), when photochemically initiated, is a chain reaction, in which the rate-determining step is the reaction $D_2 + Cl \rightarrow DCl + D$. Quantum yields of from 2 to 19 have been observed. A comparison of the proportions at the photostationary state with those at thermal equilibrium indicates that absorption by HCl is stronger than by DCl in the region 2000-2150 A.[157] Deuterobenzene (C_6D_6) may also be prepared by an exchange reaction between benzene and deuterium chloride, using aluminium chloride as catalyst,[158] and a range of partially deuterated benzenes by the decomposition of corresponding Grignard reagents by deuterium chloride.[159]

REACTION WITH ORGANIC COMPOUNDS

Discussion of the wide field of reactions of hydrogen chloride with organic compounds is not relevant here, but the breakdown of certain naturally occurring materials may be mentioned. The degradation of cellulose in the absence of water by hydrogen chloride in the liquid phase is not accompanied by swelling, and the lattice state is not affected, so that the process has been used to relate the chemical breakdown of natural and artificial fibres with the structure and lattice state of the fibres.[160] When solid rubber is exposed to gaseous hydrogen chloride at 25° and 1 atm. pressure, in the presence of the vapour of a rubber solvent, 30% of chlorine may be introduced in 50 hours. When vulcanized rubber is treated under similar conditions, 28% of chlorine is introduced in 30 hours; the product differs from that with unvulcanized rubber in that it is insoluble in benzene and chloroform, and resistant to decomposition in ultra-violet light.[161] The breakdown of potato starch by 2 N-hydrochloric acid has been examined from the point of view of the structure of the particles formed.[162] Gelatin and hydrogen chloride show chemical combination to the extent of 110 mg. HCl per gram of gelatin. On prolonged contact the gelatin darkens and decomposes and the hydrolysis products react further with hydrochloric acid.[163-165]

REACTION WITH METALS

The vapours of sodium and potassium metals react with hydrogen chloride with displacement of hydrogen atoms. The reactions of atomic sodium with hydrogen chloride and deuterium chloride proceed according to the equations $Na + HCl \rightarrow NaCl + H$, and $Na + DCl \rightarrow NaCl + D$. The rates of these reactions have been measured by the diffusion flame method; the activation energies calculated from these rates are 6,100 and 6,400 kg.-cal. respectively. The difference between these values, 300 kg.-cal., is approximately equal to the difference between the zero point energies of hydrogen chloride and deuterium chloride in the initial and transition states.[166,167] The mechanism of these reactions has been considered in the light of probability and classical collision theory.[168,169] A considerable amount of investigation has been carried out on the rates of solution of pure metals, impure metals and alloys in hydrochloric acid. In reactions involving metal surfaces, the rate of reaction is determined primarily by the rate at which the reactive species in solution can reach the metal surface. This diffusion is in turn influenced by the products of reaction, so that the rates of such reactions depend upon the rate at which the acid solution is stirred, or on the rate at which the metal specimen is rotated in the solution. Many of the quantitative studies are of value for comparative purposes only, since they were not carried out under exactly similar conditions of stirring, and cannot be related to the mechanisms of the metal-solution reaction. In such cases, quantitative measurements of reaction rates are not normally quoted below. The influence of speed of rotation of specimen on reaction rate is shown clearly by the results for zinc and magnesium[170] given in Table LVI.

TABLE LVI.- EFFECT OF ROTATION SPEED ON RATE OF SOLUTION OF ZINC AND MAGNESIUM IN HYDROCHLORIC ACID

Rate of Rotation r.p.m.	Zn dissolved (mg./cm.^{2}/5 min.)	Mg dissolved (mg./cm.^{2}/5 min.)
500	2·0	0·4
1000	3·0	0·56
1500	3·85	0·73
2000	4·55	0·87
3000	5·8	1·20
4000	7·3	1·52
5000	8·5	1·82

The zinc cylinder was 1·88 cm. long, 2·44 cm. in diameter, immersed in 0·0142 N-hydrochloric acid containing 0·05 molar potassium nitrate as depolarizer, at 25°; the magnesium cylinder was 2·5 cm. long, 2·16 cm. in diameter, immersed in 0·0071 N-acid at 25°. The reaction rate shows no sign of becoming constant even at the highest rotation speeds, and diffusion of active species to the surface is clearly the rate-determining process. It is important in measurements of this type that the metal surface should move with respect to the solution; measurements in which the containing vessel, rather than the specimen, was agitated suggested that the reaction rate between magnesium and hydrochloric acid became constant at rotation speeds exceeding 220 r.p.m.[171] The mean value of the 10° temperature coefficient of reaction rate, $k_{25°}/k_{15°}$, is 1·29; this value is typical of diffusion processes rather than of chemical reaction.[170] Consistent with this, the reaction rate is inversely proportional to the viscosity of the medium. A zinc cylinder was rotated at 4000 r.p.m. in a solution of 0·007 N-hydrochloric acid (containing 0·05 molar potassium nitrate as depolarizer); the viscosity of the acid alone (η_0) was altered by the addition of sugar, and the rates are shown in Table LVII.[170]

TABLE LVII.- INFLUENCE OF VISCOSITY ON THE RATE OF SOLUTION OF ZINC IN HYDROCHLORIC ACID

Concn. of added sugar (molar)	η_0/η	Zn dissolved (mg./cm.^{2}/5 min.)
0·0	1	3·58
0·3	0·71	2·68
0·6	0·55	2·00
0·9	0·38	1·45
1·2	0·27	0·94
1·5	0·17	0·61

Depolarizers (such as potassium nitrate, or hydrogen peroxide) appreciably increase the reaction rate (Table LVIII).[170]

Somewhat different features arise in the magnesium reaction when the hydrochloric acid is dissolved in a mixture of methyl alcohol and water. The reaction is first order with respect to hydrochloric acid concentration over the concentration range studied (0·005 M. to 0·087 M.) and over the temperature range −60° to 25°. The temperature coefficient is approximately 1·5 and the energy of activation 4·5 kg.-cal.; the mean rate constant is 1·5 at 25° and 0·61 at −60°. These values, and the profound effect of rotation speed on reaction rate, indicate that the reaction is again diffusion controlled. The presence of depolarizers such as potassium nitrate or nitroethane has a

TABLE LVIII. - INFLUENCE OF DEPOLARIZERS ON THE RATE OF SOLUTION OF ZINC IN HYDROCHLORIC ACID

	Zn dissolved at 1600 r.p.m. (mg./cm.^{2}/5 min.)	
HCl concn. (N)	(a) no depolarizer present	(b) solution containing 0·05 M-KNO_3 or 0·04 M-H_2O_2
0·004	0·58	0·80
0·012	0·65	2·60
0·02	0·83	4·20

relatively negligible effect on reaction rate.[172] The reaction rates of magnesium in solutions of deuterium chloride in deuterium oxide are identical with those for hydrogen chloride in water at acid concentrations higher than 0·05 M., but at lower concentrations the rate in deuterium oxide is rather higher. The electrode potential of magnesium in a $DCl-D_2O$ solution is 0·11 - 0·14 V. more negative than in $HCl-H_2O$ solutions.[173]

The velocity of reaction of sodium amalgam with hydrochloric acid, determined by measuring the quantity of hydrogen evolved, is proportional to the concentration of acid, but has no relation to the composition of the amalgam. The velocity increases by a factor of 1·17 with each 10° rise in temperature.[174] The reaction velocity with metallic lithium has also been determined.[175] The corrodibility of a magnesium-tin alloy in hydrochloric acid increases with the proportion of tin present, reaching a maximum corresponding to the compound Mg_2Sn. The rate then decreases with further increase in tin content. With aluminium-magnesium alloys also there is a close relation between the reaction rate with hydrochloric acid and the phase diagram of the alloy.[176]

The action of hydrochloric acid on aluminium presents a complex picture. Very pure aluminium is slow to dissolve in 2 N-acid, but dissolves more quickly in 5 - 10 N-acid. At higher acid concentrations a protective salt covering slows the reaction again.[177,178,181] The reaction proceeds in three stages: an initial passive period, then a period during which reaction velocity increases to a maximum value, and finally a period of constant or only slowly decreasing reaction velocity.[181,185] With impure aluminium, the reaction rates broadly depend upon the five factors discussed below:-

(*a*) The percentage of impurity: when the total percentage of impurity is increased from 0·002 to 0·8%, the solution rate in 20% hydrochloric acid is increased by a factor of 30,000.[177]

(*b*) The nature of the impurity: platinum, iron and copper greatly accelerate the reaction rate, nickel, gold and mercury exert a smaller effect, while cadmium and silicon are without effect. The addition of as little as 6 × 10^{-8} g. of platinum salt to 5 N-hydrochloric acid accelerates the solution of aluminium.[178] A range of aluminium samples of different grades of purity has been similarly studied.[179 181] With samples in the purity range 99·5 to 99·99%, the rate of solution was found to vary exponentially with hydrochloric acid concentration (in the dilute range) and to vary linearly with the concentration of aluminium chloride added to the solution.[180]

(*c*) The distribution of the impurity: the solid solutions which metallic impurities form with aluminium are the less homogeneous the more quickly the metal is cooled, and under these conditions the rate of solution increases.[182] The rate can also fluctuate during the course of the reaction as a greater or smaller number of particles of impurity are exposed to attack as the surface is dissolved away.[179]

(*d*) The formation of local electrical cells: the rate of solution varies with the ease with which such cells are set up and thus on the extent to which the impurities are separated from the main bulk of the metal.[178,183]

(*e*) The film of oxide almost invariably present on the surface of the metal.[180,184]

The effect of mechanical treatment of the aluminium influences the rate of attack by hydrochloric acid; the rates with annealed and hammer hardened,[182] cold rolled and annealed,[188] rolled,[185] cast[182] and heated and quenched aluminium[179,183] have been compared. The metallic structure of highly purified aluminium also affects its attack by hydrochloric acid. Immersion in 10% acid for 25 – 30 days leads to solution of metal at the grain boundaries; the rate of attack at the grain boundaries differs from that at the crystal faces, and therefore depends to some extent on the crystal orientation.[189] Kinetic studies show that the rate of solution of pure aluminium in hydrochloric acid is only slightly dependent upon the rate of stirring of the specimen, and the temperature coefficient of reaction is 1·7 to 2·4 per 10° temperature rise.[186] The suggestion has been made that undissociated HCl molecules take part in the reaction, since the addition of aluminium chloride to the solution depresses dissociation but increases the reaction rate. However, this is not consistent with the fact that the rate of solution of aluminium in a 4 N. solution of acid in absolute alcohol (in which the acid will be less dissociated than in water) is less than in the corresponding aqueous solution;[187] it is difficult to deduce reaction mechanisms from experiments involving different media, since the diffusion rates at the surface will vary with the physical properties of the medium.

Thallium metal dissolves in hydrochloric acid; it has a negative heat of reaction (–0·954 kg. cal.) and no hydrogen is evolved.[190] Many of the transition metals react with hydrochloric acid; they will be discussed in the order in which they appear in the Periodic Table. Lanthanum and cerium dissolve more quickly in concentrated than in dilute acid, although the reverse is true for lanthanum (and aluminium) amalgam.[187] Titanium is only slowly dissolved by hot, concentrated hydrochloric acid: annealing increases its resistance, and annealed titanium is resistant up to 5% acid concentration at 35°, 3% at 60°, and 1% at 100°. Zirconium resists corrosion in a wide range of acid concentrations.[191] Niobium has a high resistance to dilute acid, but is attacked by the hot concentrated acid, whereas tantalum appears to be resistant at all concentrations.[192] In 10 N-acid, chromium dissolves at first slowly, but on longer immersion reaches a constant solution rate which is the higher the greater is the acid concentration. At 40°, the induction period is less than one minute. Up to concentrations of 7·75 N. the solution rate is said to be independent of rate of stirring. The electrode potential (H scale) is 0·59 ± 0·01 V., and this is also practically independent of stirring rate. These facts, together with the observation that the 10° temperature coefficient is greater than 2, indicates that diffusion is not the rate-determining step in the case of chromium. In hydrochloric acid stronger than 10 N. the solution rate increases with stirring rate.[193] In the vapour phase chromium reacts with hydrogen chloride according to the equation $\mathrm{Cr\ (solid)} + 2HCl \rightarrow CrCl_2 + H_2$. The equilibrium constant K_p for the reverse of this reaction was found by passing a gaseous mixture of hydrogen and hydrogen chloride over heated chromium metal, and analysing the condensate; for $CrCl_2$ (gas), K_p is 2·5 at 879° and 2·0 at 930°, and for $CrCl_2$ (liquid), K_p is 6×10^{-3} at 879° and 12×10^{-3} at 930°.[194] Molybdenum and tungsten are scarcely attacked by hydrochloric acid up to 30% concentration at room temperature, or by boiling 10% acid, but are not resistant to boiling 20% acid.[195,196]

Most of the work on the attack of hydrochloric acid on iron is concerned with the effect of other added metals on the corrosion resistance (see page 470) and only a limited number of measurements have been made with the pure metal.[197-199] Table LIX shows the variation in rate of solution of iron with period of immersion in 0·5 N-hydrochloric acid.[199]

TABLE LIX. - RATE OF SOLUTION OF IRON IN 0·5 N-HYDROCHLORIC ACID

Loss in wt. of iron (g./square metre)	0·97	1·14	1·56	2·96	4·06
Immersion period (mins.)	30	60	90	240	360

With varying acid concentration, an approximately linear relation exists between the solution rate and the activity of the acid.[197] The microcalorimetric method has been applied to the study of the influence of acid concentration and surface character on the thermal effects of dissolving pure (Armco) iron in hydrochloric acid.[200] If oxide films are removed from the surface of iron by preliminary pickling in N-hydrochloric acid, the subsequent initial solution rate in the acid is increased, but coarse filing of the surface gives rise to a much higher initial solution rate. High purity Armco iron has a consistently higher solution rate than soft iron.[201] Examination of the metal surface by electron diffraction shows that when iron is treated with cold concentrated hydrochloric acid, the surface carries a film of the oxide Fe_3O_4 or γ-Fe_2O_3; treatment with hot dilute acid gives an almost pure iron surface, with only a slight indication of oxide formation.[202] The solution rate of iron is appreciably reduced when the acid contains dissolved stannous chloride. This inhibitory effect diminishes as the concentration of hydrochloric acid is increased, and is insignificant at acid concentrations exceeding 5 N.[203] The presence of gelatin, starch or saponin in solution has a protective effect on the iron; a porous gel-like film is formed on the metal which retards the passage of ions and lowers the rate of solution.[204] The presence of traces of hydrogen chloride in a moist atmosphere accelerates the rusting of iron, and this rapid rusting continues after the iron is removed from contact with the acid. The ferric chloride initially formed is believed to have a catalytic action, and to assist rusting by the formation of intermediate chloro-hydroxy complexes.[205]

Although the platinum metals are not readily attacked by hydrochloric acid, platinum black or sponge will dissolve completely if stirred in hydrochloric acid at high air pressure.[206] The rate of solution increases with increase in acid concentration, pressure and temperature. Platinum, palladium, iridium and rhodium will dissolve in hydrochloric acid if hydrogen peroxide is present, especially if the pressure is increased; this is no doubt due to initial attack on the metal by chlorine liberated by oxidation of hydrochloric acid by the peroxide. Above 200° the rhodium and iridium solutions decompose, redepositing the metal.[206] When platinum black is used as a catalyst in the oxidation of hydrogen chloride to chlorine by air, the side reaction $Pt + Cl_2 + HCl \rightarrow H_2PtCl_6$ also occurs to a small extent. Other platinum metals act in an analogous manner.[207]

Copper evolves hydrogen with concentrated hydrochloric acid, and electrode potentials in this system have been measured.[208] Attack by hydrochloric acid is facilitated by the ability of copper to form the ions $CuCl_2^-$, $CuCl_3^{2-}$ and $CuCl_3^-$. The equilibrium constants for the reaction $Cu^+ + 2Cl^- \rightleftharpoons CuCl_2^-$, and $Cu^+ + 3Cl^- \rightleftharpoons CuCl_3^{2-}$ are 5×10^{-4} and 1×10^{-4}.[208] Hydrogen chloride gas attacks copper, with liberation of hydrogen. The addition of one molecule of ammonia to fifteen molecules of hydrogen chloride increases the reaction rate a hundredfold, owing to the ease of formation of the complex NH_3-Cu-Cl.[209] In boiling concentrated hydrochloric acid solutions, silver is not appreciably attacked below the air-line. Protective films, probably of silver chloride, are formed which are stable when the metal is completely immersed and the acid saturated with silver chloride. However, there is appreciable attack in the vapour phase, and if the metal is partly immersed in the concentrated acid there is strong corrosion at the air-line.[210] Gold dissolves in concentrated hydrochloric acid in the presence of oxidizing agents such as nitric acid (as in aqua regia) or hydrogen peroxide.[206] The reaction is again no doubt due to the initial production of free chlorine. The electrochemical behaviour of gold in solutions of chloroauric acid ($HAuCl_4$) in hydrochloric acid has been studied. The strong polarization in these solutions can be decreased considerably by increase in temperature and acid concentration.[211]

Reference has already been made to the influence of stirring rate, solution viscosity and depolarizers on the rate of solution of zinc in hydrochloric acid. The rate of solution of pure zinc in 0·5 N-acid is lowered by the addition to the solution of hydrocyanic acid, which appears to react directly with the metal. Thiocyanic acid, potassium thiocyanate and carbon disulphide catalyze the reaction, but thiourea and sulphur dioxide are without effect.[212] As with many other metals, the rate of solution of zinc decreases as the metal is highly purified; this has been demonstrated for exceptionally pure zinc of 99·9999% purity.[213] The products of corrosion of zinc have been examined by electron diffraction study of the metal surface. Using a normal solution of hydrochloric acid, the corrosion product consists of minute crystals of zinc chloride which have well-developed planes bonded by van der Waals' forces. Using 10 N-acid, the zinc chloride crystals are larger and do not show association in planes.[214] Rates of corrosion of an aluminium-zinc alloy have been measured over the concentration range 1 – 37% of hydrochloric acid; the corrosion rate is a maximum at 25% acid.[215] Cadmium metal dissolves very slowly in dilute hydrochloric acid, but at a readily measurable rate in solutions above 6 N. There is an initial induction period, but if the sample is activated by immersion for 24 hours in concentrated acid the induction period almost vanishes and the metal begins to react at a constant velocity. In the absence of dissolved oxygen, the reaction is first order with respect to acid concentration. From the change in rate at different chloride ion concentrations (produced by adding sodium chloride) the reaction $CdCl^{2-} + CdCl^+ \rightarrow 2CdCl_2 + Cl^-$ has been postulated as the rate-determining step.[216] However, the rate of solution is not independent of dielectric constant, viscosity or stirring rate, so that diffusion is also a major factor. A surprising feature is the large negative temperature coefficient of reaction; each 5° rise in temperature decreases the reaction rate by a factor of 10.[216] The surface of the cadmium becomes coated with a black deposit at higher temperatures, which is ascribed to the dissociation of the ionic species $CdCl^+$. When cadmium is alloyed with small quantities of platinum (0·5 – 1·0%) or gold (1·0%) the solubility rate is increased. Alloying with 0·8% of copper alters the rate very little.[217] Although mercury is not attacked by hydrochloric acid in the absence of oxygen, calomel and hydrogen peroxide are produced in the presence of oxygen: $2Hg + 2HCl + O_2 \rightarrow Hg_2Cl_2 + H_2O_2$, and $2Hg + 2HCl + H_2O_2 \rightarrow Hg_2Cl_2 + 2H_2O$. In the initial stages of the reaction the calomel and hydrogen peroxide are produced in equivalent quantities. If the acid concentration is maintained and the mercury well shaken, the consumption of oxygen is constant. The unit HO_2, and an active layer of hydrogen on the metal surface are postulated as probable intermediates in the reaction.[218]

The thermodynamics of solutions of the transuranic elements in hydrochloric acid have recently been investigated.[219-221] The heat of solution of plutonium metal in 6 N-hydrochloric acid is -141·64 kg.-cal./mol.[219]

CORROSION

Since iron has been the metal most readily available for construction and storage purposes, much investigation has been carried out on the influence of other added metals on the corrosion of various forms of hard and mild steel, and cast iron, by hydrochloric acid. Such additions normally increase the resistance of iron to corrosion, but to widely differing extents, and several such alloys are claimed to be completely resistant. Quantitative studies on the corrosion of iron alloys by hydrochloric acid have been made on alloys containing nickel,[222,224] silicon,[222,223,230] manganese,[222] chromium,[223,225] silicon and manganese,[222] chromium and nickel,[223] molybdenum and silicon,[229,230] molybdenum, silicon and nickel,[230] and on alloys containing nickel, chromium and copper together with silicon,[227] manganese and antimony,[226] and molybdenum and antimony.[228] With both cast iron and steel, the corrosion increases regularly with acid concentration.[222] Cast iron containing 34% of chromium is stable against hydrochloric acid of not over 0·5% concentration at temperatures up to 60°, whereas on reducing the chromium content to 14%, the alloy is no longer resistant to this acid.[225] The corrosion of steels containing much silicon is accelerated more by increase in temperature than by increase in acid concentration; resistance to corrosion in the presence of several metals is not additive, since adding molybdenum to silicon steels can increase the stability towards hydrochloric acid tenfold, whereas adding nickel has little effect.[230] Tungsten has an effect similar to that of molybdenum. The resistance of iron, manganese, molybdenum or tungsten, separately or mixed, to hydrochloric acid is enhanced by alloying with one or more of the Group 5 elements arsenic, antimony or bismuth.[231] Electron diffraction studies of the surface of iron–tungsten and iron–molybdenum alloys which are resistant to attack on immersion in hydrochloric acid show that the surface becomes covered compactly with fine crystals of tungsten or molybdenum dioxide.[232,233] *X*-Ray diffraction has been used to study the processes involved in the corrosion of iron, nickel, cadmium and zinc by air containing hydrochloric acid vapour.[234]

Nickel alloys show pronounced resistance to hydrochloric acid. Nickel-base alloys containing carbon, silicon, iron, chromium, manganese, molybdenum, tungsten, copper and aluminium are 20 times more resistant than lead, and certain of the alloys can withstand the action of boiling concentrated acid.[235] Alloys containing 30% of molybdenum (or molybdenum and tungsten), but no chromium, are little attacked by the pure acid, but are readily attacked in the presence of oxidizing agents such as ferric chloride, nitric acid or dissolved oxygen. This is prevented by the addition of chromium, and alloys containing more than 15% Cr and 7% Mo are resistant to attack by hydrochloric acid even in the presence of oxidizing agents.[195] Corrosion rates for 42 nickel alloys containing the metals tantalum, titanium, zirconium, and vanadium in addition to those mentioned above, have been measured and compared.[196] Monel metal (30% Ni, 70% Cu) is resistant to hydrochloric acid at concentrations up to 5%, but higher acid concentrations are very corrosive, especially when hot.[236,237]

The corrosion of tantalum–molybdenum alloys varies with the alloy composition. Molybdenum-rich alloys are attacked by concentrated hydrochloric acid at 50°, whereas corrosion is negligible in alloys containing more than 50 atomic percent. of tantalum.[238] The corrosion of cadmium–magnesium alloys by 0·01 N-hydrochloric acid also varies in type with change in alloy composition.[239] Silver alloys (e.g. 80% Ag, 20% Al + Mn) have a strong resistance to corrosion,[240,241] and the protection of iron, steel and copper by plating with platinum, gold or silver alloys has been considered.[242]

The degree of corrosion of metals by hydrochloric acid may be reduced by the use of inhibitors dissolved in the acid. The phenolic compounds obtained by alkaline extraction of crude petroleum inhibit the corrosion of metals, particularly steel.[243] Quinoline (0·5%) has this inhibiting effect on the corrosion of iron at 20°, but the effect is not observed at higher temperatures;[244,245] the solution of brass in hydrochloric acid is retarded by the addition of quinoline and potassium ferrocyanide.[244]

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SECTION XVI

COMPOUNDS OF CHLORINE WITH BROMINE AND IODINE

By N. N. GREENWOOD

BROMINE MONOCHLORIDE

After more than a century of controversy (Mellor, II, 115) the existence of bromine monochloride is now firmly established.[1,2] The compound has a characteristic absorption spectrum in the ultra-violet, visible and micro-wave regions, as well as an individual Raman spectrum. Evidence for the existence of bromine monochloride is also given by a study of the reactions of mixtures of chlorine and bromine with organic compounds.

Bromine monochloride may be prepared by direct reaction of chlorine and bromine either in the gas phase (equation 1) or in carbon tetrachloride solution (equation 6). The free halogens themselves may be used for reaction (1) or they may be generated in the system by reactions of the type (2), (3) and (4). Reaction (10) has also been used to prepare the compound.

Bromine monochloride is an orange-red gas which is appreciably dissociated into its elements:-

$$BrCl \rightleftharpoons \tfrac{1}{2}Br_2 + \tfrac{1}{2}Cl_2 \qquad (1)$$

Because of this dissociation and the fact that chlorine, bromine and bromine monochloride appear to form continuous solid solutions with each other, the phase diagram of the system gives no information about the compound.[1,3] Estimates of the equilibrium constant for reaction (1) vary considerably. Early work on the absorption of visible light by chlorine, bromine and their gaseous mixtures[4] suggested that $K = p_{Br_2}^{1/2} \cdot p_{Cl_2}^{1/2}/p_{BrCl} = 0{\cdot}354$ to $0{\cdot}363$. Similar measurements[5] gave values between 0·316 and 0·469 at room temperature and, from experiments at five temperatures between 0° and 230°C., it was concluded that

$$\log K = 0{\cdot}09 - 660/(4{\cdot}57T), \pm 0{\cdot}05.$$

Later work improved the correction for light absorption by bromine monochloride at the wave-lengths used, but failed to produce consistent results. The values obtained by the extinction coefficient method are summarized in Table I.

The dissociation constant of bromine monochloride has also been determined from the high-temperature equilibria between metal halides and the halogens. Thus a study of the equilibrium:-

$$\tfrac{1}{2}Cl_2\,(g) + KBr\,(l) = KCl\,(l) + \tfrac{1}{2}Br_2\,(g) \qquad (2)$$

at 800°C. led to values of the dissociation constant of bromine monochloride between 0·336 and 0·376 with a mean value of 0·349 ± 0·014.[10] Other molten-salt pairs which have been used at 500° and 800°C. are NaBr–NaCl, AgBr–AgCl and $PbBr_2$–$PbCl_2$.[11] At lower temperatures equilibrium concentrations of chlorine and bromine have been maintained by the dissociation of nitrosyl chloride and bromide:-[12]

$$NOCl\,(g) = NO\,(g) + \tfrac{1}{2}Cl_2\,(g) \qquad (3)$$
$$NOBr\,(g) = NO\,(g) + \tfrac{1}{2}Br_2\,(g) \qquad (4)$$

TABLE I - DISSOCIATION CONSTANTS FOR $BrCl\ (g) = \frac{1}{2}Br_2\ (g) + \frac{1}{2}Cl_2\ (g)$

$$K = p_{Br_2}^{1/2} \cdot p_{Cl_2}^{1/2} / p_{BrCl}$$

Method	t°C*	K	Ref.
extinction coefficient	r.t.	0·359 ± 0·005	4
extinction coefficient	r.t.	0·393 ± 0·077	5
extinction coefficient	r.t.	0·347 ± 0·015	6,7
extinction coefficient	28	0·327 ± 0·003	8
extinction coefficient	r.t.	0·380 ± 0·004	9
system $(KCl,KBr)_l(Br_2,Cl_2,BrCl)_g$	800	0·349 ± 0·014	10
system $(AgCl,AgBr)_l(Br_2,Cl_2,BrCl)_g$	500	0·364	11
and other salt pairs	800	0·347 ± 0·007	
system $(NOCl,NOBr,Br_2,Cl_2,BrCl)_g$	190	0·385 ± 0·015**	12
spectroscopic	25	0·132	13
spectroscopic	25	0·3376	14

* r.t. = room temperature.

** mean of 21 values between 0·331 and 0·436 at temperatures between 159° and 218°C.

From the known equilibrium constants of reactions (3) and (4), together with the total pressure and composition of the system, the dissociation constant of bromine monochloride can be calculated. The method suffers from the large corrections which are necessary for gas imperfections especially at low temperatures, and uncertainties from this cause obscure the slight trend of values with temperature. In one particular experiment at 100°C., the uncorrected value of $K = 2{\cdot}21$ was reduced to 0·316 when gas imperfections had been allowed for. The correction is less serious at 218°C. and a typical correction reduced the dissociation constant from 0·449 to 0·424. The results obtained from these various equilibrium systems are summarized in Table I. The values are very similar to those obtained at room temperature by the extinction coefficient method.

A third method of calculating the dissociation constant of bromine monochloride has been the application of statistical mechanics to spectroscopic data.[13,14] Complete data are not available, however, and estimated values for the anharmonicity constant and internuclear distance were used. In addition, there is no spectroscopic value for the heat of dissociation of bromine monochloride; thermochemical values vary widely and the derived dissociation constants reflect the particular value of the heat of dissociation adopted. Of all the values listed in Table I, the figure given by Ref. 14, although not unexceptionable, is preferred. Table II lists the complete results[14] for the equilibrium (1) between room temperature and 2000°K. The calculations use 430 cm^{-1} for the fundamental frequency; values for the anharmonicity constant and internuclear distance were estimated as 1·684 cm^{-1} and 2·11 A. (the accepted[15] micro-wave value is 2·138 A.) and the heat of dissociation at absolute zero was taken to be −233 g.-cal. $mole^{-1}$. The results refer to the ideal gaseous state with normal isotopic abundances at 1 atm. pressure, and were obtained on the rigid-rotator, harmonic-oscillator approximation neglecting nuclear spin entropy and the entropy of isotopic mixing. Table II also lists values for the heat content and free energy changes in reaction (1) as well as the corresponding figures for the dissociation of bromine monochloride into atoms:-

$$BrCl = Br + Cl \qquad (5)$$

It will be seen that the equilibrium constant for dissociation into molecular

TABLE II. - DISSOCIATION OF BROMINE MONOCHLORIDE[14]

$BrCl = \frac{1}{2}Br_2 + \frac{1}{2}Cl_2$

T°K.	$\Delta H^\circ/T$	$\Delta G^\circ/T$	$K = p_{Br_2}^{\frac{1}{2}} \cdot p_{Cl_2}^{\frac{1}{2}} / p_{BrCl}$
	(g.-cal.deg.$^{-1}$mole^{-1})		
298·16	0·80286	2·1578	0·3376
300	0·80122	2·1527	0·3385
400	0·59370	1·9542	0·3740
500	0·47205	1·8356	0·3971
600	0·39203	1·7574	0·4130
700	0·33376	1·6913	0·4290
800	0·29405	1·6590	0·4340
900	0·26214	1·6244	0·4416
1000	0·23675	1·6002	0·4470
1200	0·19967	1·5653	0·4549
1400	0·17303	1·5319	0·4626
1600	0·15498	1·5096	0·4678
1800	0·14109	1·5000	0·4701
2000	0·12995	1·4781	0·4753

$BrCl = Br + Cl$

T°K.	$\Delta H^\circ/T$	$\Delta G^\circ/T$	$K = p_{Br} \cdot p_{Cl} / p_{BrCl}$
	(g.-cal.deg.$^{-1}$mole^{-1})		
298·16	175·12	151·16	$9{\cdot}142 \times 10^{-34}$
300	174·06	150·09	$1{\cdot}580 \times 10^{-33}$
400	130·98	106·51	$5{\cdot}278 \times 10^{-24}$
500	105·12	80·273	$2{\cdot}860 \times 10^{-18}$
600	87·869	62·728	$1{\cdot}954 \times 10^{-14}$
700	75·539	50·158	$1{\cdot}092 \times 10^{-11}$
800	66·286	40·702	$1{\cdot}272 \times 10^{-9}$
900	59·085	33·328	$5{\cdot}203 \times 10^{-8}$
1000	53·321	27·412	$2{\cdot}777 \times 10^{-6}$
1200	44·673	18·507	$9{\cdot}023 \times 10^{-5}$
1400	38·495	12·104	$2{\cdot}263 \times 10^{-3}$
1600	33·862	7·3397	$2{\cdot}488 \times 10^{-2}$
1800	30·258	3·5080	$1{\cdot}711 \times 10^{-1}$
2000	27·373	0·4741	$7{\cdot}878 \times 10^{-1}$

chlorine and bromine varies but little with temperature, whereas the dissociation into atoms depends strongly on temperature: it is negligible at room temperature but above 1650°C. it predominates over dissociation into molecules. The results show that at room temperature the degree of dissociation of bromine monochloride is 40·3% and that this increases to 46·4% at 500°C. For temperatures below 25°C. the equilibrium constant and free energy change for reaction (1) may be estimated from the relations: $-4{\cdot}578T \log K = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 239 + 1{\cdot}355T$.

The heat of formation of bromine monochloride from its elements has not been satisfactorily determined owing to its small magnitude and the wide variation in experimental values for the equilibrium constant at different temperatures. Values suggested for the heat of formation according to the reverse of equation (1) include 0,[12] −54,[10] −135,[12] −138,[11] −156,[5] −170,[9] −300,[16] −375,[5] and −660[5] g.-cal. mole^{-1}. A critical survey of the relevant data, together with a partial evaluation of spectroscopic data[12] suggests that, at the absolute zero, $\Delta H_f^\circ = -233$ g.-cal. mole^{-1} is the most acceptable value. The thermodynamic constants of bromine monochloride, based on this figure and calculated on the assumptions mentioned earlier, have been evaluated.[14] Values for the heat capacity, entropy, free energy and heat content of bromine monochloride are set out in Table III. In using these figures and those in Table II it should be remembered that the retention of four or five significant figures merely serves to establish a consistent set of values at the various temperatures and in no way reflects the absolute accuracy of the quantities involved which may be uncertain even in the second significant figure. These results supersede the earlier data:-[17,18]

$$C_p^\circ = 8{\cdot}92 - 0{\cdot}50 \times 10^5 T^{-2}$$
$$H_T^\circ - H_{298\cdot16}^\circ = 8{\cdot}92T + 0{\cdot}50 \times 10^5 T^{-1} - 2827 \quad (298^\circ < T^\circ\text{K.} < 1600^\circ)$$
$$S_{298\cdot16}^\circ = 57{\cdot}36 \pm 0{\cdot}10 \text{ g.-cal. mole}^{-1}\text{ deg.}^{-1}$$

TABLE III. - HEAT CAPACITY, ENTROPY, FREE ENERGY AND HEAT CONTENT OF BROMINE MONOCHLORIDE[14] IN G.-CAL. MOLE^{-1} DEG.$^{-1}$

T°K.	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$(H^\circ-H_0^\circ)/T$
298·16	8·384	57·339	49·783	7·556
300	8·390	57·390	49·829	7·558
400	8·625	59·840	52·039	7·801
500	8·754	61·779	53·800	7·980
600	8·833	63·383	55·267	8·116
700	8·886	64·749	56·527	8·222
800	8·925	65·938	57·630	8·308
900	8·955	66·991	58·612	8·378
1000	8·979	67·936	59·499	8·437
1200	9·018	69·577	61·051	8·531
1400	9·050	70·969	62·366	8·603
1600	9·077	72·179	63·519	8·660
1800	9·103	73·250	64·542	8·708
2000	9·126	74·210	65·461	8·749

The existence of bromine monochloride in gaseous mixtures of chlorine and bromine, which was established by spectrophotometric measurements[4,5] and by an analysis of its band spectrum in the vacuum ultra-violet,[19] has been confirmed by measurements in carbon tetrachloride solutions.[20-23] Typical results are shown in Fig. 1 which represents the molar absorbency of solutions of chlorine, bromine and their equimolar mixtures.[23] The observed curve for bromine monochloride is quite different from that obtained by adding the curves for chlorine and bromine. Similar measurements on solutions containing three moles of chlorine to one mole of bromine indicate that the hypothetical compound bromine trichloride is completely dissociated into the monochloride and chlorine under these conditions.[21]

In carbon tetrachloride solution the absorption maximum of bromine monochloride is at 370 mμ[20,23] (or 380 mμ[21]) and the maximum molar absorbency index is 135.[23] Estimates of the equilibrium constant for reaction (6) vary as widely as those for the corresponding gas-phase dissociation (1):-

$$\text{BrCl (in CCl}_4) = \tfrac{1}{2}\text{Br}_2 \text{ (in CCl}_4) + \tfrac{1}{2}\text{Cl}_2 \text{ (in CCl}_4) \qquad (6)$$

The original results[20] ranged from 0·37 to 0·70 with a mean value of 0·52 ± 0·11 for $K = [\text{Br}_2]^{\frac{1}{2}}[\text{Cl}_2]^{\frac{1}{2}}/[\text{BrCl}]$. This value was later[5] reduced to 0·42 and

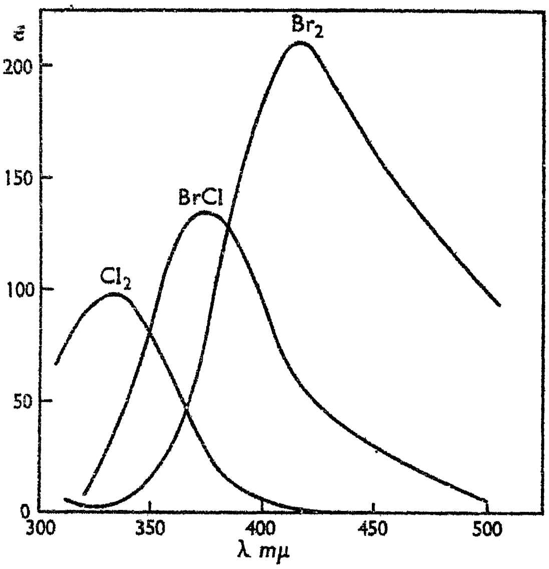


Fig. 1. MOLAR ABSORPTION OF CHLORINE, BROMINE AND BROMINE MONOCHLORIDE

subsequent work gives the dissociation constant as 0·381 ± 0·008, corresponding[23] to a degree of dissociation of 43·2% at 25°C. Similar measurements at 15° and 10°C. gave essentially the same results.[23]

The thermodynamic constants of bromine monochloride in carbon tetrachloride have been evaluated from calorimetric measurements.[16] When the most recent value for the dissociation constant is used, the heat content, free energy and entropy of formation according to the reverse of reaction (6) become $\Delta H^\circ_{298\cdot16} = -312$ g.-cal., $\Delta G^\circ_{298\cdot16} = -572$ g.-cal., and $\Delta S^\circ_{298\cdot16} = 0\cdot872$ g.-cal. deg.$^{-1}$

The Raman frequency of bromine monochloride in carbon tetrachloride has been detected by using the helium 6678 A. line as exciting radiation.[24] The first vibrational frequency lies at 428 ± 2 cm.$^{-1}$ which is close to the value of 430 cm.$^{-1}$ used for the spectroscopic calculations in the vapour state.

Precise determinations of the m.p. and b.p. of bromine monochloride are prevented by its pronounced dissociation. Values obtained from melting-point and boiling-point curves at equi-atomic ratios of chlorine and bromine are not to be regarded as constants of the pure compound; rather are they equilibrium temperatures for phase changes of the type:-

$$(Cl_2 + Br_2 + BrCl)_{\text{solid solution}} \rightarrow (Cl_2 + Br_2 + BrCl)_{\text{liquid solution}}$$

For this reason, values[25] of m.p. -66° and b.p. +5°C. do little more than indicate approximately the temperatures between which dissociating bromine monochloride exists as a liquid phase. Thus, the vapour pressure of a liquid of overall composition Br:Cl = 1:1 reaches 760 mm. at -5°, but a temperature of +36°C. is required before the vapour above the liquid attains the same composition.[26] By low-pressure distillation of equal parts of chlorine and bromine between -70° and -90°, it has been claimed that bromine monochloride may be obtained as an ochre-yellow solid which melts sharply at -54° to a dark orange-red liquid.[27] The vapour pressure of bromine monochloride prepared in this way is presented in Table IV.

TABLE IV. - VAPOUR PRESSURE OF SOLID AND LIQUID BROMINE MONOCHLORIDE[27]

t°C.	−87	−82	−75	−69	−62	−57	−51	−50
p mm.	-	0·5	1·6	3·0	7·1	13·4	21·9	25·5

From the linear plots of log p against $1/T$°K. it would appear that the latent heats of sublimation, evaporation and fusion are approximately 10·7, 8·3 and 2·4 kg.-cal. mole^{-1}; the extrapolated 'b.p.' is +1°C., and the triple point pressure 14 mm. However, when the preparation is warmed above −50° a small amount of solid bromine separates on the surface of the liquid and the vapour also dissociates rapidly.[27] Extrapolation of the data in Table II suggests that, even at −83°C., the degree of dissociation of bromine monochloride vapour is 35%.

The dipole moment of bromine monochloride has been estimated as 0·57 ± 0·02 D. from the micro-wave spectrum of the gas.[15] The same measurements give the bond length Br–Cl as 2·138 A.[15] The percentage ionic character of the bond is calculated to be 5 − 6% from nuclear quadrupole coupling constants;[28,29] an estimate[28] from electronegativity differences gives 10%.

The normal electrode potential of bromine monochloride at 25·00°C. is 1·1548 ± 0·0005 V. in 6·079 N. aqueous hydrochloric acid, referred to a hydrogen electrode in the same solution.[30] In 3·997 N-hydrochloric acid the normal potential is 1·221 ± 0·001 V. The measurements were made with cells of the type:-

$$(-\mathrm{Pt,H_2|H_2|HCl + Cl_2 + BrCl + Br^-|PtIr} +).$$

If the concentration of bromine is 1 M., then 2·4% of the bromine is converted into bromide ion and bromine monochloride when the acid strength is 6 N., and 2·8% is converted in 4N-hydrochloric acid. If the bromine concentration is 0·01 M., then the conversion is 20% in 6 N. and 18·5% in 4N-hydrochloric acid, and this percentage continues to increase until, at infinite dilution of bromine, the reaction approaches completion.[30] For both concentrations of hydrochloric acid, the equilibrium constant for bromine monochloride is given by $K = [\mathrm{Br_2}]^{\frac{1}{2}}[\mathrm{Cl_2}]^{\frac{1}{2}}/[\mathrm{BrCl}] = 0{\cdot}0179 \pm 0{\cdot}0005$. This is much smaller than the values for the free gas or its solution in carbon tetrachloride and implies that bromine monochloride is more stable in hydrochloric acid solution ($\alpha = 3{\cdot}5\%$) than as a gas ($\alpha = 40{\cdot}3\%$) or as a solution in carbon tetrachloride ($\alpha = 43{\cdot}2\%$). For reaction (7):-

$$(\tfrac{1}{2}\mathrm{Br_2} + \mathrm{Cl^-} = \tfrac{1}{2}\mathrm{Cl_2} + \mathrm{Br^-})_{\text{in aq. HCl}} \qquad (7)$$

the equilibrium constant in 6 N-hydrochloric acid is:-

$$K = [\mathrm{Cl_2}]^{\frac{1}{2}}[\mathrm{Br^-}]/\{[\mathrm{Br_2}]^{\frac{1}{2}}[\mathrm{Cl^-}]\} = 1{\cdot}73 \times 10^{-6};$$

in 4 N-acid $K = 2{\cdot}36 \times 10^{-6}$ [30] The hydrolysis constant of bromine monochloride in water[31] is $2{\cdot}94 \times 10^{-5}$ at 0°C.

CHEMICAL PROPERTIES OF BROMINE MONOCHLORIDE

When chlorine and bromine are mixed several seconds elapse before the colour change is completed.[20] The reaction is also slow in carbon tetrachloride solution but appears[20] to be instantaneous in water, or in ether or chloroform even at −78°C. The reaction is photosensitive[4,8,9] and, in the absence of light, may take several days to attain equilibrium.[8] Kinetic studies show[32] the dark reaction to be bimolecular and homogeneous with an activation energy of about 14 kg.-cal. mole^{-1}. Later work implies that the wall has a marked effect on the velocity of the dark reaction.[9] The quantum yield of the light reaction[9] is $(1-2) \times 10^3$.

Bromine monochloride tetrahydrate, $BrCl,4H_2O$, has been prepared[33] as orange-red crystals by the action of chlorine gas on liquid bromine under water at 0°C. The compound can be recrystallized from water at 14°C. It is stable at temperatures as high as 10° above the decomposition points of chlorine hexahydrate (9°C.) and bromine hexahydrate (6°C.). Bromine monochloride forms[34] a 1:1 addition compound with pyridine, $C_5H_5N,BrCl$, m.p. 107 - 108°C. The compound is obtained from carbon tetrachloride solutions as white crystals which are stable in dry air but decompose slowly in a moist atmosphere. Pyridine-bromine monochloride is decomposed by hot ethanol or acetone.[34] Bromine monochloride also forms addition compounds with the simple halide ions to give polyhalides (q.v.). The free energy changes and equilibrium constants of the following reactions in aqueous solution have been evaluated:[35]

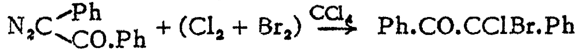
$$BrCl(aq.) + Cl^-(aq.) = BrCl_2^-(aq.);\ -\Delta G^\circ_{298} = 3{\cdot}3 \text{ kg.-cal.};\ K = 260 \text{ l.mole}^{-1}$$
$$BrCl(aq.) + Br^-(aq.) = Br_2Cl^-(aq.);\ -\Delta G^\circ_{298} = 3{\cdot}8 \text{ kg.-cal.};\ K = 620 \text{ l.mole}^{-1}$$
$$BrCl(g) + Cl^-(aq.) = BrCl_2^-(aq.);\ -\Delta G^\circ_{298} = 4{\cdot}3 \text{ kg.-cal.};\ K = 1{\cdot}5 \times 10^{-3} \text{ atm.}^{-1}$$
$$BrCl(g) + Br^-(aq.) = Br_2Cl^-(aq.);\ -\Delta G^\circ_{298} = 5{\cdot}78 \text{ kg.-cal.};\ K = 5{\cdot}8 \times 10^{-5} \text{ atm.}^{-1}$$

The electron acceptor strength (acid strength) of bromine monochloride is considerably less than that of iodine monochloride but is slightly greater than that of iodine monobromide.[35]

The products of reactions of mixtures of chlorine and bromine with organic compounds have long been adduced as evidence for the existence of bromine monochloride (Mellor,II,115). The addition of equimolar mixtures of chlorine and bromine to cinnamic acid and its derivatives in non-hydroxylic solvents gives α-bromo-β,β-chlorophenylpropionic acid and its derivatives rather than the dichloro- or dibromo-derivatives.[36] The reaction, more rapid than that of either chlorine or bromine alone, is bimolecular.[36] Similar experiments with phenylpropiolic acid, $Ph.C\vdots C.CO_2H$, in carbon tetrachloride solution at 0°C. in the dark yield[37] only the chlorobromo-addition product, $Ph.CCl{:}CBr.CO_2H$. The reaction is again bimolecular and more rapid than that with chlorine or bromine separately.[37] When acetic acid is used as a solvent the results are more complicated.[38] Bromine monochloride in this solvent adds to cinnamic acid according to third order kinetics and simultaneous substitution side reactions occur. Comparison of rates, however, shows that bromine monochloride reacts some 400 times more rapidly than does bromine itself.[38]

With aliphatic diazo compounds, mixtures of chlorine and bromine react rapidly and energetically to give the chlorobromo-product.[39] Diazoacetic ester in carbon tetrachloride at 0° yields ethyl chlorobromoacetate (8), and benzoylphenyldiazomethane gives chlorobromodesoxybenzoin (9):-

$$N_2CH.CO_2Et + (Cl_2 + Br_2) \xrightarrow{CCl_4} ClBrCH.CO_2Et \qquad (8)$$



$$N_2C\begin{matrix}\nearrow Ph\\ \searrow CO.Ph\end{matrix} + (Cl_2 + Br_2) \xrightarrow{CCl_4} Ph.CO.CClBr.Ph \qquad (9)$$

A careful analysis of the products of this last reaction leads to the conclusion that, under the conditions of the experiment, bromine monochloride is 20% dissociated into chlorine and bromine.[39] This implies a value of 0·125 for the equilibrium constant of reaction (6) at 0°C.

A convenient source of bromine monochloride for addition to carbon-carbon double bonds is the reaction between N-bromoacetamide and concentrated hydrochloric acid:-[40]

$$CH_3.CO.NHBr + HCl = CH_3.CO.NH_2 + BrCl \qquad (10)$$

The structures of the chlorobromides obtained suggest that bromine monochloride adds to double bonds according to a polar mechanism, in which positive bromine, Br^+, is transferred to the double bond to form a complex bromonium ion which is attacked by the chloride ion Cl^- to give the product.[40]

IODINE MONOCHLORIDE

Preparation.

Iodine monochloride is usually prepared by the oxidation of an iodide in hydrochloric acid solution or by direct combination of the elements. It is also formed by the metathesis of chlorides with compounds containing unipositive iodine (1), or the displacement of positive iodine from an ion-exchange resin (2).[41]

$$\mathrm{ICN + HCl = HCN + ICl} \qquad (1)$$

$$\mathrm{I^+ \text{ (on resin)} + KCl = K^+ \text{ (on resin)} + ICl} \qquad (2)$$

The oxidants that have been used to prepare solutions of iodine monochloride in hydrochloric acid include potassium permanganate,[42] chlorine water,[43,44] dichloramine-*T*[45,46] and potassium iodate.[47-51] Thus, a molar solution of iodine monochloride was prepared by dissolving 110·7 g. of potassium iodide and 71·3 g. of potassium iodate in 833 ml. of 6 N-hydrochloric acid and making the volume up to 1 l. with water.[48] The reaction may be used for the potentiometric determination of iodate in 1 - 2 N-hydrochloric acid. There are two inflexions in the titration curve, indicating that the iodate is first reduced quantitatively to iodine monochloride and then to iodine:-[51]

$$\mathrm{2KI + KIO_3 + 6HCl = 3ICl + 3KCl + 3H_2O} \qquad (3)$$

$$\mathrm{3KI + 3ICl = 3KCl + 3I_2} \qquad (4)$$

The direct combination of chlorine and iodine may be carried out either in a solvent or without one. Chlorine has been added to a suspension of iodine in water or dilute hydrochloric acid[43,44] or to a solution of iodine in acetic acid[38] or chloroform.[52] A solution of iodine monochloride in carbon tetrachloride may be prepared by passing pure, dry chlorine into a solution of iodine in carbon tetrachloride until yellow crystals of iodine trichloride begin to separate, and then aspirating dry air through the solution to remove excess chlorine.[53] Alternatively, for small concentrations (10^{-2} - 10^{-3} molar), both halogens may be dissolved in separate portions of carbon tetrachloride and the solutions mixed.[22]

In the absence of a solvent, chlorine may be passed into a flask containing iodine until the increase in weight indicates only a slight excess of iodine. The product is then distilled at atmospheric pressure.[54] This method suffers from the disadvantage that iodine monochloride is partially dissociated at its boiling point. For the preparation of highly purified iodine monochloride, a weighed amount of solid iodine is added to about twice its molar equivalent of liquid chlorine in a weighed flask which is cooled in a bath of solid carbon dioxide and ether. The product is allowed to warm to room temperature in order to liberate any uncombined chlorine. The flask and its contents are then weighed and the amount of iodine required for stoicheiometry added. The impure product is allowed to stand in the liquid state for twenty-four hours and is then purified by two or three fractional crystallizations of the melt in an apparatus protected from atmospheric moisture.[55-57]

PHYSICAL PROPERTIES OF IODINE MONOCHLORIDE

Recent determinations of the m.p. of iodine monochloride give values similar to those previously reported (Mellor, II, 117). Values have varied between 26·9°C. and 27·3°C.[58-68] but the most reliable measurements on highly purified samples give 27·18°,[69] 27·19°[55] and 27·20°,[70] the last figure being the usually accepted m.p. The b.p. is less significant because of partial thermal dissociation and its value is generally quoted as a range of temperatures, e.g. 104° - 105°C.;[59] 100° - 102°C.[61] Extrapolation of the v.p. curve above 70°C. leads[55,71] to a b.p. of 97°C.

The vapour pressure of iodine monochloride as a solid, as a supercooled liquid, and as a normal melt has been measured[55,56,60,71,76] between -15° and 70°C. The relation between the v.p. of molten iodine monochloride (mm. Hg) and the absolute temperature from 273°K. (supercooled) to 343°K. has been given as:-

$$\log_{10} p \text{ mm.} = 8{\cdot}5038 - 2079{\cdot}7/T$$

which corresponds to a heat of vaporization ($\Delta H_{\text{vap.}}$) of 9·52 kg.-cal. mole^{-1} and a Trouton constant ($\Delta S_{\text{vap.}}$) of 25·5 g.-cal. deg.$^{-1}$ mole^{-1}. The v.p. so calculated lies between 5 mm. and 275 mm. and is some 1 - 10 mm. higher than the preferred values given in Tables V and VI.[60] These correspond to the equations:-

$$\text{solid } \alpha\text{-ICl} : \log_{10} p \text{ mm.} = 10{\cdot}108 - 2578/T$$
$$\text{liquid ICl} : \log_{10} p \text{ mm.} = 8{\cdot}761 - 2174/T$$

TABLE V. - VAPOUR PRESSURE OF IODINE MONOCHLORIDE (SOLID AND SUPERCOOLED LIQUID)[60]

t°C.	-15	-10	-5	0	5	10	15	20	25	27·3
p mm. (sol.)	1·2	2·0	3·1	4·6	6·8	9·9	14·3	20·4	28·3	33·2
p mm. (liq.)	-	-	-	-	-	12	16·3	21·9	29·3	33·2

TABLE VI. - VAPOUR PRESSURE OF LIQUID IODINE MONOCHLORIDE

t°C.	27·3	30	35	40	45	50	55	60	65	70
p mm. (ref. 60)	33·2	38·4	50·4	64·4	84·5	107·1	-	-	-	-
p mm. (ref. 55)	-	-	48·0	62·5	81·0	103·6	131·9	166·0	209·0	261·7

The relations lead to the following values of the heats of sublimation, vaporization and fusion:-

$\Delta H_{\text{subl.}}$ = 11·80 kg.-cal. mole^{-1}; $\Delta H_{\text{vap.}}$ = 9·95 kg.-cal. mole^{-1};
$\Delta H_{\text{fus.}}$ = 1·85 kg.-cal. mole^{-1}; Trouton constant, 26·7 g.-cal. deg.$^{-1}$ mole^{-1}.

These values are taken to supersede those calculated from the last line of Table VI: $\Delta H_{\text{vap.}}$ = 10·22 kg.-cal. mole^{-1}; Trouton constant 27·3 g.-cal. deg.$^{-1}$ mole^{-1}.

The density of the unstable (β) modification of solid iodine monochloride is 3·66 ± 0·01 g. ml.$^{-1}$ at 0°C., corresponding to a molar volume of 44·3 ml.[72] The values for α-iodine monochloride are 3·86 ± 0·01 g. ml.$^{-1}$ and 42·1 ml., respectively. The $\beta \rightarrow \alpha$ transformation is therefore accompanied by a contraction of 2·2 ml. (approx. 5%). These figures, however, may not be reliable as the same author finds the density of the liquid at 29° to be 3·10 g. ml.$^{-1}$, which is some 3% lower than other published values:- d_4^{35} = 3·184,[66] 3·192,[73] 3·199;[66] d_4^{45} = 3·159,[66] 3·169;[66] d_4^{50} = 3·166.[65,73] This large spread of values suggests that the density of pure liquid iodine monochloride has yet to be determined satisfactorily.

The dynamic viscosity, η, has been reported for a series of temperatures;[67] (alternative values are given in parentheses[73]):-

t°C.	25	35	45	50
η centipoise	3·729	3·058 (3·052)	2·550	2·255 (2·015)

From the linear graph of log η against the reciprocal of the absolute temperature (excluding the values at 50°C.), the activation energy of viscous flow may be estimated as 3·6 kg.-cal. mole^{-1}.

The specific electrical conductivity, κ, of pure molten iodine monochloride has attracted much attention recently and arises from self-ionic dissociation according to the scheme:-[2]

$$2ICl = I^+ + ICl_2^- \qquad (5)$$

The thirteen published values[55,61-66,68,70] for 35°C. fall in the range $(4{\cdot}52-5{\cdot}70) \times 10^{-3}$ ohm^{-1} cm.$^{-1}$, and there is a similar variation for other temperatures:- 25°C. $(4{\cdot}46-4{\cdot}96) \times 10^{-3}$;[61,63,70] 45°C. $(4{\cdot}61-8{\cdot}3) \times 10^{-3}$;[61-63,66,68,70,74] 50°C. $(4{\cdot}53-5{\cdot}84) \times 10^{-3}$;[62,64,65,70] and 55°C. $(4{\cdot}42-5{\cdot}14) \times 10^{-3}$ ohm^{-1} cm.$^{-1}$.[62,70,75] The conductivity of highly-purified, vacuum-recrystallized iodine monochloride as measured in a sealed cell at 1000 cycles/sec. a.c. over the temperature range 25°- 120°C. is given in Table VII.[70] Under these conditions, the values of the conductivity are accurately reproducible and alter reversibly with temperature, but traces of moisture increase the value irreversibly.[55,70] The molar conductivity, μ, (the product of specific conductivity and molar volume) is also tabulated. There is a curious maximum in both the specific and the molar conductivities at about 40°C.[70] (A flat maximum between 50° and 70°C. has also been reported).[62] This has been ascribed to the interaction of two opposing effects, viz., the increase in mobility of the ions with temperature on the one hand, owing to a decrease in viscosity, and a decrease in their number on the other, owing to the thermal instability of the polyhalide ion (cf. equation 5):-

TABLE VII. - ELECTRICAL CONDUCTIVITY OF MOLTEN IODINE MONOCHLORIDE[70]

t°C.	26·75	30·6	34·45	39·9	45·1	49·7	55·1	59·8	64·8	69·0	79·3	81·8	91·4	101·0	113·0	122·0
$10^3\kappa$ ohm^{-1} cm.$^{-1}$	4·403	4·519	4·593	4·637	4·611	4·541	4·415	4·270	4·057	3·810	3·271	3·068	2·667	2·471	2·043	1·817
μ ohm^{-1} cm.^{2}	0·2217	0·2309	0·2355	0·2392	0·2392	0·2366	0·2314	0·2250	0·2149	0·2027	0·1760	0·1655	0·1455	-	-	-

$$ICl_2^- = ICl + Cl^-; \quad Cl^- + I^+ = ICl.$$

The degree of self-ionic dissociation in molten iodine monochloride at 35°C. has been estimated as about 1%.[70] Because of the concurrent thermal dissociation of iodine monochloride into chlorine and iodine (see Table VIII) there is no decomposition potential for the electrolysis of the molten compound.[70] The conductivity of solid iodine monochloride just below its m.p. is about one hundredth of that of the liquid.[2]

The molar diamagnetic susceptibility of molten iodine monochloride is $-56{\cdot}8 \times 10^{-6}$ cgsm. units.[77] (An alternative value for the liquid at 12°C. is $-54{\cdot}6 \times 10^{-6}$ cgsm. units).[78] The parachor, calculated from measurements on a solution of the interhalogen in ethanol, is 135·83 which corresponds with the calculated value for a purely covalent bond I-Cl.[79] More delicate estimates of the deviation from covalency, calculated from electronegativity differences and from nuclear quadrupole coupling constants, indicate that the percentage ionic character of the bond I^+Cl^- is 25%.[28] (A value of 9% has also been suggested).[29]

The dipole moment of gaseous iodine monochloride has been calculated from the pressure and temperature dependence of the dielectric constant between 0 - 140 mm. and 60°- 160°C. According to the assumptions made and the method of extrapolation, the estimated dipole moment is 0·5 or 0·8 D.[80,81] A more reliable value of 0·65 ± 0·06 D. has been obtained by micro-wave techniques.[82] When the dipole moment of iodine monochloride is measured in solution, a much larger value is obtained (1·47 - 1·49 D.) owing to incipient solvolytic ionization of the compound[81] (see page 490).

The bond distance I–Cl, r_e = 2·32069 A. obtained from the micro-wave spectrum of the gas [82,83] is in substantial agreement with the older value from band spectrum data, r_e = 2·3150 A.[84] The mean value of the internuclear distances of the parent halogens is 2·328 A.

The thermodynamic functions of iodine monochloride have been determined experimentally from measurements on the equilibrium between chlorine, iodine and iodine monochloride over a range of temperatures.[71] In one series of measurements between 370° and 470°C., the pressure of chlorine was controlled by the dissociation of barium hexachloroplatinate (equation 6); in a second series between 140° and 180°C. the reaction between iodine and nitrosyl chloride and the concurrent dissociation of nitrosyl chloride were used (equations 7 and 8).

$$BaPtCl_6 = BaCl_2 + Pt + 2Cl_2 \qquad (6)$$
$$2NOCl + I_2 = 2NO + 2ICl \qquad (7)$$
$$2NOCl = 2NO + Cl_2 \qquad (8)$$

The results were miscalculated[16] but lead finally to the values given in Table VIII. The values of ΔH were estimated to be correct to within about ±5%.

TABLE VIII. - FREE ENERGY AND HEAT OF FORMATION, AND ABSOLUTE ENTROPY OF IODINE MONOCHLORIDE AT 25°C.

Reaction $\frac{1}{2}I_2 + \frac{1}{2}Cl_2 = ICl$	$-\Delta G^\circ_{298\cdot16}$	$-\Delta H^\circ_{298\cdot16}$	$S^\circ_{298\ 16}$ (ICl) (g.-cal. deg.$^{-1}$ mole^{-1})
	(kg.-cal. mole^{-1})		
(g) + (g) = (g)	3·653	3·125	59·6 (g)
(s) + (g) = (g)	1·370	−4·313	-
(s) + (g) = (l)	3·214	5·207	33·4 (l)
(s) + (g) = (s)	3·234	7·875	24·6 (s)

From the relation $\Delta S = (\Delta H - \Delta G)/T$ and the figures in Table VIII, the entropy of formation of gaseous iodine monochloride from the gaseous elements is 1·77 g.-cal. deg.$^{-1}$ mole^{-1}. These direct thermochemical results agree fairly well with the spectroscopic values for the gaseous reaction:- $-\Delta G^\circ_{298\cdot16}$ = 3·879 kg.-cal. mole^{-1}; $-\Delta H^\circ_{298\cdot16}$ = 3·461 kg.-cal. mole^{-1}; $\Delta S^\circ_{298\cdot16}$ = 1·40 g.-cal. deg.$^{-1}$ mole^{-1}; $S^\circ_{298\cdot16}$ = 59·2 g.-cal. deg.$^{-1}$ mole^{-1}.[71] More recently, the free energy change in this reaction has been calculated as 3·71 kg.-cal. mole^{-1}, from which the degree of thermal dissociation is 0·38% at 25°C.; at the b.p. (100°C.) this dissociation is 1·1%.[2] These values replace the earlier estimates of 0·42% and 1·58% respectively.[71] The standard free energy and heat of formation have also been recalculated and the values obtained, $-\Delta G^\circ_{298\ 16}$ = 3·25 kg.-cal. mole^{-1} and $-\Delta H^\circ_{298\cdot16}$ = 8·04 kg.-cal. mole^{-1},[2] are probably nearer the true values than are those given in the last line of Table VIII.

The heat capacity, entropy, free energy and heat content of iodine monochloride in the ideal gaseous state at 1 atm. pressure have been evaluated from spectroscopic data on the rigid-rotator, harmonic-oscillator approximation, with appropriate contributions for anharmonicity.[14] The results, which are assembled in Table IX, include neither nuclear-spin entropy nor the entropy of isotopic mixing. The same spectroscopic data, in conjunction with those for chlorine and iodine, have been used[14] to calculate the heat content changes, free energy changes and equilibrium constants for the dissociation of iodine monochloride into atoms and into molecules at temperatures up to 1727°C. (see Table X). The results show that the dissociation into molecular chlorine and iodine predominates at temperatures below about 1500°C. and that the degree of dissociation of iodine monochloride, which has been seen to be 1·1% at the b.p., reaches 10% at about 500°C.

TABLE IX. - HEAT CAPACITY, ENTROPY, FREE ENERGY AND HEAT CONTENT OF IODINE MONOCHLORIDE[14] IN G.-CAL. DEG.$^{-1}$ MOLE^{-1}

T°K.	C_p°	S°	$-(G^\circ - E_0^\circ)/T$	$(H^\circ - E_0^\circ)/T$
298·16	8·492	59·123	51·468	7·655
300	8·497	59·175	51·514	7·661
400	8·697	61·650	53·753	7·898
500	8·805	63·604	55·535	8·069
600	8·871	65·216	57·018	8·198
700	8·917	66·587	58·289	8·297
800	8·950	67·780	59·403	8·377
900	8·977	68·835	60·393	8·442
1000	8·999	69·782	61·286	8·497
1200	9·035	71·426	62·843	8·584
1400	9·065	72·821	64·168	8·650
1600	9·092	74·033	65·330	8·704
1800	9·118	75·106	66·357	8·748
2000	9·141	76·068	67·281	8·787

TABLE X - DISSOCIATION OF IODINE MONOCHLORIDE[14]

	ICl = I + Cl			ICl = ½I$_2$ + ½Cl$_2$		
T°K.	$\Delta H^\circ/T$ (g.-cal. deg.$^{-1}$ mole^{-1})	$\Delta G^\circ/T$	$K = p_{\text{I}} p_{\text{Cl}}/p_{\text{ICl}}$	$\Delta H^\circ/T$ (g.-cal. deg.$^{-1}$ mole^{-1})	$\Delta G^\circ/T$	$K = p_{\text{I}_2}^{1/2} \cdot p_{\text{Cl}_2}^{1/2}/p_{\text{ICl}}$
298·16	168·74	145·19	1·854 × 10^{-32}	11·186	12·507	1·848 × 10^{-3}
300	167·72	144·16	3·123 × 10^{-32}	11·117	12·437	1·914 × 10^{-3}
400	126·20	102·17	4·695 × 10^{-23}	8·3304	9·6598	7·743 × 10^{-3}
500	101·29	76·889	1·571 × 10^{-17}	6·6597	7·9943	1·790 × 10^{-2}
600	84·668	59·983	7·779 × 10^{-13}	5·5475	6·8845	3·129 × 10^{-2}
700	72·788	47·870	3·453 × 10^{-11}	4·7524	6·1070	4·627 × 10^{-2}
800	63·870	38·760	3·381 × 10^{-9}	4·1601	5·4978	6·288 × 10^{-2}
900	56·926	31·654	1·208 × 10^{-7}	3·6987	5·0353	7·935 × 10^{-2}
1000	51·415	25·954	2·127 × 10^{-6}	3·3799	4·6657	9·558 × 10^{-2}
1200	43·010	17·373	1·596 × 10^{-4}	2·7779	4·1104	1·264 × 10^{-1}
1400	37·030	11·213	3·544 × 10^{-3}	2·3839	3·7101	1·546 × 10^{-1}
1600	32·539	6·578	3·651 × 10^{-2}	2·0904	3·4049	1·803 × 10^{-1}
1800	29·042	2·955	2·261 × 10^{-1}	1·8625	3·1893	2·009 × 10^{-1}
2000	26·244	0·0442	9·780 × 10^{-1}	1·6803	3·0005	2·209 × 10^{-1}

SOLUTIONS CONTAINING IODINE MONOCHLORIDE

There is an arbitrary dividing line between what may be considered as a variation of physical properties of a given solute in a series of solvents on the one hand, and the chemical interaction of the solvent and solute on the other. This sub-section will discuss the properties of solutions of iodine monochloride in aqueous hydrochloric acid, the electrochemistry of iodine monochloride in non-aqueous solvents, the spectrophotometric properties of solutions, and finally, the thermodynamic functions of iodine monochloride when dissolved in carbon tetrachloride. The next sub-section will deal with systems in which iodine monochloride behaves as an ionizing solvent. Here, there is greater emphasis on chemical interaction, and several addition compounds and reaction products have been isolated. The concluding sub-section deals with the purely chemical properties of iodine monochloride.

Iodine monochloride forms a stable, yellow solution in aqueous hydrochloric acid from which it cannot be extracted with organic solvents such as carbon tetrachloride, benzene or nitrobenzene, in which it is normally readily soluble.[47,53,85,86] This is due to the formation of the dichloro-iodide ion.[85,86]

$$\mathrm{ICl + Cl^- = ICl_2^-} \qquad (9)$$

Other suggestions, that the colour change and stability are due to ionization of the interhalogen ($\mathrm{ICl = I^+ + Cl^-}$),[47] or to the formation of undissociated hydrogen dichloroiodide $\mathrm{HICl_2}$,[59] fail to explain the following facts. (*a*) The addition of iodine monochloride to N-hydrochloric acid, until the solution is 0·14 M. in iodine monochloride, diminishes the electrical conductivity by about 0·7%[85] (*i.e.* $\mathrm{Cl^-}$ is replaced by $\mathrm{ICl_2^-}$; complete ionization into $\mathrm{I^+ + Cl^-}$ would raise the conductivity markedly, whereas the formation of undissociated $\mathrm{HICl_2}$ would remove both $\mathrm{H^+}$ and $\mathrm{Cl^-}$ from solution and thereby decrease the conductivity appreciably). (*b*) The electrolysis of a 1·6 M-solution of iodine monochloride in 1 N-hydrochloric acid does not result in migration of iodine to the cathode (*i.e.* the solution contains no $\mathrm{I^+}$).[85] (*c*) Aqueous sodium chloride may be used instead of hydrochloric acid.[59] As the position of equilibrium of reaction (9) is independent of the hydrochloric acid concentration between 0·2 N. and 10 N.,[59] it is clear that the polyhalide ion is but little dissociated. The equilibrium constant for the reverse of equation (9) has been estimated from the distribution ratio of iodine monochloride between carbon tetrachloride and 0·4 N-hydrochloric acid at 25·0°: $K = \mathrm{[ICl][Cl^-]/[ICl_2^-]} = (6{\cdot}0 \pm 0{\cdot}5).10^{-3}$ mole/l.; $\Delta G = 3{\cdot}04$ kg.-cal. mole^{-1}.[53] Results obtained in other solvents are summarized in Table XIV and indicate that in these dissociation is even less pronounced than in aqueous systems. The degree to which iodine monochloride undergoes the alternative reaction of dissociation into its elements depends slightly on the normality of the hydrochloric acid and is about 1% of the corresponding dissociation of the interhalogen in the vapour phase (cf. Table X); $K = \mathrm{[I_2]^{1/2}[Cl_2]^{1/2}/[ICl]} = 1{\cdot}27 \times 10^{-5}$ in 2 N-HCl, $1{\cdot}51 \times 10^{-5}$ in 4 N-HCl, and $1{\cdot}98 \times 10^{-5}$ in 6 N-HCl.[53] In the absence of hydrochloric acid (or a chloride), iodine monochloride rapidly hydrolyses to hydrochloric and hypoiodous acids; the latter compound then disproportionates into iodic acid and iodine which is precipitated. For the primary hydrolysis:-[53]

$$\mathrm{ICl + H_2O = H^+ + Cl^- + HOI,} \qquad (10)$$
$$K = \mathrm{[H^+][Cl^-][HOI]/[ICl]} \simeq 10^{-4}\ \text{moles}^2\ \text{l.}^{-2}$$

The overall hydrolysis may be represented[53] by equation (11):-

$$\mathrm{5ICl + 3H_2O = 5H^+Cl^- + H^+IO_3^- + 2I_2} \qquad (11)$$
$$K = \mathrm{[H^+]^6[Cl^-]^5[I_2]^2[IO_3^-]/[ICl]^5} \simeq 10.^{-7}$$

The decomposition potential of an aqueous solution of iodine monochloride (0·35 mole/l.) between platinum electrodes has been given[87] as 0·27 V. at 15°, but it seems certain that the solute would be appreciably hydrolysed. For a similar reason it is difficult to interpret precisely the standard electrode potential, $E^\circ_{\mathrm{I/ICl}} = 1{\cdot}116$ V. which has been measured by means of the cells:-

(+I | aq. ICl | N-KCl | normal calomel electrode −) and
(+Pt | aq. ICl | N-KCl | normal calomel electrode −).[87]

This result, in conjunction with the similarly obtained values $E^\circ_{\mathrm{I/IBr}} = 1{\cdot}102$ V. and $E^\circ_{\mathrm{I/ICl_3}} = 1{\cdot}032$ V. would place the iodine cation with the noble metals in the electrochemical series.

The electrochemistry of iodine monochloride in several non-aqueous solvents has been studied.[88-91] The compound is an electrolyte when dissolved in dry nitrobenzene,[88-91] glacial acetic acid,[88,89] dichloroacetic acid[2] or ethyl ether,[2] but is a non-conductor in carbon tetrachloride, trichloroethylene, pentachloroethane, silicon tetrachloride, stannic chloride or antimony pentachloride.[2] This duality of character is reflected in the colour of the solutions which may be either yellow or red-brown, and in the varying chemical reactivity of iodine monochloride in the various solvents (see page 490). The specific electrical conductivity in nitrobenzene at 18° decreases from $8{\cdot}18 \times 10^{-4}$ ohm^{-1} cm.$^{-1}$ (1 mole ICl/6·62 mole $C_6H_5NO_2$) to $2{\cdot}84 \times 10^{-4}$ ohm^{-1} cm.$^{-1}$ (1 mole ICl/35·89 mole $C_6H_5NO_2$).[91] At the same temperature, the conductivity of iodine monochloride in anhydrous acetic acid decreases from $8{\cdot}057 \times 10^{-4}$ ohm^{-1} cm.$^{-1}$ (3·31 wt.-% ICl) to $0{\cdot}187 \times 10^{-4}$ ohm^{-1} cm.$^{-1}$ (9·34 wt.-% ICl).[55] Iodine monochloride shows no decomposition potential when its conducting solutions are electrolyzed.[88] This absence of polarization at both electrodes is presumably due, as in the case of the pure molten compound itself, to the slight thermal dissociation of iodine monochloride into the parent halogens. The electrolysis of iodine monochloride in glacial acetic acid between platinum electrodes results in the migration of iodine to both the cathode and the anode and the concurrent migration of two equivalents of chlorine to the anode.[89] This indicates ionic dissociation according to equation 12.

$$2ICl = I^+ + ICl_2^- \qquad (12)$$

The positive iodine cation, which has only six valency electrons, is stabilized by donor-acceptor interaction with the solvent.[2,47] Preliminary results on the electrolysis of iodine monochloride in nitrobenzene appeared to be more complicated,[89] but when silver electrodes were used the results were consistent with the ionization (12).[90]

Non-aqueous solutions of iodine monochloride may be either red-brown or yellow, depending on the solvent used.[59] The red-brown solutions show maximum absorption at 455 ± 10 mμ whereas for the yellow solutions, this maximum is displaced by about 100 mμ towards shorter wave-lengths ($\lambda_{max.}$ = 355 ± 10 mμ). The relevant data are summarized in Table XI. In addition to the solvents listed in the table, solvents which give red-brown solutions include carbon disulphide, silicon tetrachloride, tin tetrachloride, antimony pentachloride, hexane, ethyl bromide, trichloroethylene, pentachloroethane, chlorobenzene, benzene, toluene and xylene; yellow solutions are formed by amyl acetate, acetic anhydride, acetone and pyridine.[2,59] This dichroism of

TABLE XI. - VISIBLE ABSORPTION SPECTRUM OF IODINE MONOCHLORIDE IN VARIOUS SOLVENTS

Solvent	$\lambda_{max.}$ mμ	$\epsilon_{max.}$	Colour	Refs.
(Pure ICl gas)	470	-	red-brown	92
*cyclo*Hexane	466,(505)	165,(145)	red-brown	94,(81)
Carbon tetrachloride	460,(464)	150-2(173)	red-brown	59,93,94,(21)
Chloroform	455	150	red-brown	59
Trifluoroacetic acid	450	105,(123)	red-brown	93,(94)
Sulphuric acid (anhyd.)	442	145	red-brown	93
Ethylene dichloride	426	131,(132)	red-brown	93,(94)
Acetic acid (glacial)	360,362·5	158,138	yellow	59,93,94
Ethyl ether	359	140-160	yellow	59
Acetonitrile	359	137	yellow	94
Propiononitrile	356	142	yellow	94
Valeronitrile	357	143	yellow	94
Ethyl acetate	351	150-160	yellow	59
Trimethylcarbinol	346	188	yellow	95
Methanol	344	189	yellow	94
Ethanol	343	181	yellow	94
Hydrochloric acid (dil.)	343	273	yellow	59

iodine monochloride is precisely analogous to the well-known behaviour of iodine solutions which have as their limiting colours violet and red-brown. The same effect has also been noted for bromine and for iodine monobromide.[2,59,96] The colour change is due, primarily, to interaction of the solute with the solvent to form an addition complex which, in some instances, may dissociate ionically to give conducting solutions.[2] The degree of interaction between iodine monochloride and various solvents may be gauged from the rise in temperature which occurs when 1 ml. of the interhalogen is added to 25 ml. solvent at 25°C.: carbon tetrachloride (−2·7°), chloroform (−1·3°), ethylene dichloride (+0·2°), chlorobenzene (0·6°), water (2·0°), benzene (2·1°), glacial acetic acid (2·7°), aqueous hydrochloric acid (3·3°), ether (5·0°), 95% ethanol (5·3°) and absolute ethanol (7·5°).[130] In red-brown solutions, the absorption maximum is close to that of the pure gaseous interhalogen (470 mμ) and there is little interaction between solvent and solute; this is consistent with the nature of the solvents, none of which have appreciable electron-donor properties. However, even in such solvents, solvation is not entirely absent and there is sufficient interaction to double the apparent dipole moment of the molecule[81] (see page 485). On the other hand, yellow solutions are formed by solvents possessing an electron-donor group and this group provides the mechanism for solvation:-

$$\text{solvent} + \text{ICl} = \text{solvent:I}^{\delta+}\text{Cl}^{\delta-} \qquad (13).$$

In some instances these addition compounds are sufficiently stable to be isolated (see below). When the solvent possesses not only a donor group but also a high dielectric constant, electrolytic dissociation of the complex may ensue:-

$$\text{solvent} + 2\text{ICl} = \text{solvent:I}^{+} + \text{ICl}_2^{-} \qquad (14)$$

Under these conditions the absorption spectrum will be that of the dichloroiodide ion rather than of the unsolvated iodine monochloride molecule.[2] When a donor solvent is added to a red-brown solution of iodine monochloride in a non-solvating solvent, the colour changes to yellow and the solution becomes conducting, e.g. the addition of a trace of ethanol to a red-brown chloroform solution ($\lambda_{\text{max.}} = 455$ mμ) renders it yellow ($\lambda_{\text{max.}} = 355$ mμ)[59] and conducting.[2,96] Further, if a yellow solution, e.g. in acetic acid ($\lambda_{\text{max.}} = 360$ mμ), be heated, it turns brown ($\lambda_{\text{max.}} = 460$ mμ)[59] and at the same time the conductivity decreases.[2] This reversible effect of temperature in decreasing the conductivity is related to the thermal instability of the complex, and establishes that the conductivity is not due to impurities or to the products of a reaction with the solvent; for if either of these were the cause, the conductivity would increase with temperature, in the latter case irreversibly. The varying chemical reactivity observed for iodine monochloride in brown and in yellow solutions respectively also arises from this solvolytic ionization[2,38,97,98] and it has been suggested that the solvation complexes may serve as intermediates in aromatic halogenation reactions.[99]

The ultra-violet spectrum of solutions containing iodine monochloride depends in like fashion on the solvent chosen. When complexing solvents are used (yellow solutions) there is a pronounced absorption band at 230 mμ associated with the dichloroiodide ion and absent in the red-brown solutions.[94] In aromatic solvents mixed with carbon tetrachloride, which constitute a series of solvent systems intermediate between the two limiting classes of solvent, there is a strong band at about 300 mμ.[99] This has been ascribed to a charge-transfer spectrum of the 1:1 addition complex between the interhalogen and the hydrocarbon.[100] In this instance there is no concurrent ionic dissociation. The spectrophotometric data are summarized in Tables XII and XIII. The data may all be interpreted in terms of equations 9, 13 and 14 which are

TABLE XII. - ULTRA-VIOLET SPECTRUM OF SOLUTIONS CONTAINING IODINE MONOCHLORIDE AND RELATED EQUILIBRIUM CONSTANTS AT 25°C.[94]

Solvent	$\lambda_{max.}$	$\epsilon_{max.}10^{-4}$	$K_y = \frac{[D:I^+][ICl_2^-]}{[D:ICl]^2}$	α_y*
Acetonitrile	227	2·18	12·5	78%
Propionitrile	229	2·42	44·7†	87%†
Valeronitrile	232	-	-	-
Ethanol	227	0·74	approx. ∞	approx. 100%

* degree of ionic dissociation according to equation *y* in aged solutions.

† ref. 95 gives $K_y = 3 \cdot 10^2$, $\alpha_y = 94\%$.

TABLE XIII. - ULTRA-VIOLET SPECTRUM OF IODINE MONOCHLORIDE IN SOLVENT MIXTURES OF CARBON TETRACHLORIDE WITH AROMATIC HYDROCARBONS AND RELATED EQUILIBRIUM CONSTANTS AT 25°C.[99]

Solvent	$\lambda_{max.}$	$\epsilon_{max.}$	$K_x = \frac{[D:ICl]}{[D][ICl]}$ *
Benzene	287	8290	4·76
Toluene	294	8096	7·97
tert.-Butylbenzene	290	6330	8·70
o-Xylene	303	7075	15·4
m-Xylene	301	8340	16·0
p-Xylene	295	6860	13·4
Chlorobenzene	287	3910	2·24
Bromobenzene	289	4350	3·43

* from measurements in the visible region, acetic acid has K_x = 18·4 ± 0·7 and trifluoroacetic acid has K_x = 0·0 ± 0·9.[93] For solvents in Table XII, complexing was virtually complete, *i.e.* $K_x \simeq \infty$.[94]

rewritten here in more convenient form using the symbol D (donor) for the solvent molecule:-

$$D + ICl = D{:}ICl \qquad (x)$$
$$2D{:}ICl = D + D{:}I^+ + ICl_2^- \qquad (y)$$
$$ICl_2^- = ICl + Cl^- \qquad (z).$$

Spectrophotometric values for the equilibrium constants of these reactions, K_x, K_y, K_z at 25° are given in Tables XIII, XII and XIV respectively. Solutions of iodine monochloride in nitriles or alcohols are seen to be completely solvated according to equation (*x*) and the complex is appreciably dissociated into ions (*y*). The absorption data in Table XII should be compared with the figures obtained for the pure dichloroiodide ion itself in acetonitrile:[101] $\lambda_{max.}$ = 227 mμ; $\epsilon_{max.}$ = $5 \cdot 5 \times 10^4$. Table XIV indicates that the polyhalide ion formed in equation (*y*) is stable in nitriles but undergoes some dissociation (*z*) in hydroxylic solvents; this dissociation is virtually complete in trifluoroacetic acid, possibly because reaction *z* is followed by the elimination of hydrogen chloride according to equation 15:-[95]

$$CF_3CO_2H + Cl^- = HCl + CF_3CO_2^- \qquad (15).$$

It is to be noted, also, that in this highly acidic solvent, there is practically

TABLE XIV.- EQUILIBRIUM CONSTANTS FOR THE DISSOCIATION OF THE DICHLOROIODIDE ION AT 25°.[95]

Solvent	$K_z = [ICl][Cl^-]/[ICl_2^-]$	% dissocn. at 5×10^{-3} molar
Acetonitrile	$(5{\cdot}9 \pm 0{\cdot}7).10^{-7}$	0·6
Propionitrile	$(5{\cdot}9 \pm 0{\cdot}7).10^{-7}$	0·6
Ethylene dichloride	$(7{\cdot}1 \pm 0{\cdot}8).10^{-5}$	12
Acetic acid	$(1{\cdot}5 \pm 0{\cdot}4).10^{-4}$	17
Ethanol	approx. 10^{-3}	33
Water (ref. 51)	$(6{\cdot}0 \pm 0{\cdot}5).10^{-3}$	65
Trifluoroacetic acid	-	100

no solvation (equation *x*; Table XIII). In the mixed solvents (Table XIII) stability of the donor-acceptor complex is seen to depend on the electron-releasing properties of the hydrocarbon. This increases with increasing alkyl substitution from benzene, through toluene and *tert.*-butylbenzene, to the xylenes, and decreases when electron attracting groups, e.g. halogens, are substituted in the nucleus.

The foregoing discussion of the electrochemistry and spectrophotometric properties of non-aqueous solutions of iodine monochloride has considered only those solutions from which iodine monochloride may be recovered unchanged. In many systems (e.g. solutions in acetone or methanol) the rate of chemical reaction (chlorination of the solvent) is too rapid to permit the satisfactory determination of the physical properties.

The thermodynamic functions of iodine monochloride when dissolved in carbon tetrachloride have been calculated from the partial pressure of the interhalogen above the solution and other relevant data.[16] For mole fractions between $1{\cdot}59 \times 10^{-3}$ and $2{\cdot}03 \times 10^{-2}$ the partial pressure of iodine monochloride at 25°C. rises linearly from 0·331 mm. to 4·16 mm. The Henry's Law constant is 209 mm., which corresponds to a free energy change for reaction (16) of $-\Delta G^\circ_{298} = 0{\cdot}763$ kg.-cal. mole^{-1}. This leads to a free energy change for reaction (17) of $-\Delta G^\circ_{298} = 4{\cdot}018 \pm 0{\cdot}050$ kg.-cal. mole^{-1}, which implies an equilibrium constant of 812 and hence a degree of dissociation of iodine monochloride in carbon tetrachloride of 0·25% (compare with 0·38% for the gas phase, page 486). The heat content change for reaction (17) obtained calorimetrically is $-\Delta H^\circ_{298} = 3{\cdot}970 \pm 0{\cdot}030$ kg.-cal. mole^{-1}; whence $\Delta S^\circ_{298} = 0{\cdot}16$ g.-cal. deg.$^{-1}$ mole^{-1}. When related to chlorine and iodine in their standard states (gas and solid, respectively), the free energy and heat content of iodine monochloride in carbon tetrachloride at 25° become −2·133 and −2·835 kg.-cal. mole^{-1}, respectively, for the hypothetical state of unit mole fraction. The absolute entropy of iodine monochloride in such a solution is[16] 38·3 g.-cal. deg.$^{-1}$ mole^{-1}.

$$\text{ICl (g)} = \text{ICl (in CCl}_4\text{)} \qquad (16)$$

$$\tfrac{1}{2}\text{I}_2 \text{ (in CCl}_4\text{)} + \tfrac{1}{2}\text{Cl}_2 \text{ (in CCl}_4\text{)} = \text{ICl (in CCl}_4\text{)} \qquad (17)$$

The freezing-point curves for the system iodine monochloride-carbon tetrachloride indicate a series of solid solutions for which the liquidus is represented by a sigmoid curve.[58,102] There is a eutectic at −26·4°C. and 1·8 mole-% iodine monochloride. The components also form a metastable double-layer liquid system which has an upper critical temperature of approx. 14°C.[58,102] This unusual behaviour remains unexplained. Mixtures of iodine monochloride and acetic acid form a simple binary system in which each component depresses the f.p. of the other until a eutectic is formed at −34·5°C. with 40 mole-% iodine monochloride.[58,102]

IODINE MONOCHLORIDE AS AN IONIZING SOLVENT

The electrical conductivity of iodine monochloride at 35°C. is considerably increased when potassium chloride or ammonium chloride is dissolved in it. For example, the conductivity of an M/2 solution of potassium chloride (1 mole KCl/39 moles ICl) is 4·2 times that of the pure solvent; with an M. solution of ammonium chloride (1 mole NH_4Cl/19·5 moles ICl) the corresponding factor is 4·3.[55,56] The equivalent conductivities rise with dilution to limiting values of about 32 for potassium chloride and 26 for ammonium chloride. Other compounds which dissolve in iodine monochloride to give an enhanced conductivity include rubidium chloride,[104] cæsium chloride,[104] potassium bromide,[61,105] potassium iodide,[61,105] titanium tetrachloride,[75] vanadium tetrachloride,[75] phosphorus pentachloride,[68,75,106] antimony pentachloride,[75 106] pyridine,[64] acetamide,[63] benzamide,[65] N-diethylbenzamide,[73] and acetanilide.[73] Compounds that are but slightly soluble in iodine monochloride, or have little effect on the conductivity, include lithium chloride,[75,104] sodium chloride,[75,104] silver chloride,[75,104] copper dichloride,[104] barium chloride,[75 104] silicon tetrachloride,[75] tin tetrachloride[107] and niobium pentachloride.[75] Thionyl chloride, which is miscible with iodine monochloride in all proportions, appears to act merely as an inert diluent and progressively lowers the conductivity of the interhalogen (see Table XXVII,page 495).[75]

The solubilities of these compounds are summarized in Table XV. Little fundamental significance attaches to these values as the solubility is frequently limited either by the insolubility of the complex formed, or by the complete solidification of the system at a given concentration. Phase diagrams relating these m.p. with composition have been given for the systems of iodine monochloride with aluminium trichloride,[66] phosphorus pentachloride,[68] pyridine,[64] and benzamide.[65] Table XV does indicate, however, that the ease with which simple chlorides form polyhalides is related to the size of the cation. The chlorides of potassium, rubidium, cæsium and ammonium readily dissolve to give the dichloroiodide $MICl_2$, whereas the chlorides of the smaller cations lithium, sodium, silver and barium show little such tendency.

TABLE XV. - SOLUBILITIES IN IODINE MONOCHLORIDE AT 35°C.

Compound	Solubility g./100 g. ICl	Solubility mole %*	Ref.
Lithium chloride	<0·6	<2·2	104
Sodium chloride	<0·6	<1·6	104
Potassium chloride	5·8	11·2	104
Rubidium chloride	14·10	16·0	104
Cæsium chloride	19·9	16·1	104
Ammonium chloride	6·27	16·0	104
Silver chloride	<0·6	<0·7	104
Potassium bromide	9·33	11·28	61
Potassium iodide	6·75	6·20	61
Barium chloride	<0·6	<0·4	104
Aluminium chloride	95·4	53·71	66
Aluminium bromide	361	68·69	61
Silicon tetrachloride	'soluble'	-	75
Tin tetrachloride	'soluble'	-	75
Titanium tetrachloride	'moderately sol.'	-	75
Phosphorus pentachloride	~32·5	~20	68
Antimony pentachloride	1·9	1	106
Niobium pentachloride	'soluble'	-	75
Thionyl chloride	completely miscible	-	75
Pyridine	29	37	64
Acetamide	>85	>70	63
Benzamide	50	40	65
N-Diethylbenzamide	completely miscible	-	73

* moles of solute per 100 moles of solvent plus solute

The electrical conductivities of systems in which iodine monochloride is the solvent are presented in Tables XVI to XXVI. In general, the conductivity increases rapidly with concentration of the solute until a maximum value some 3 – 5 times that of the solvent is reached at 5 – 12 mole %. Thereafter, the conductivity diminishes as a result of the sharp increase in viscosity of the system as the solution becomes more concentrated. Exceptions are ammonium chloride, for which there is no maximum in the range studied,[55] and the halides of aluminium.[66,61] These latter solutions show a curious drop in conductivity in the range 0 – 2 mole %, after which there is a slight increase to a maximum value of 1·3 times the conductivity of the solvent. In no instance does the conductivity curve indicate the presence of known addition compounds, presumably because of the complex influence of changing density, viscosity and degree of ionic dissociation with composition in the binary systems. The results do demonstrate, however, that these solutions have high equivalent conductivies which are in many cases comparable with those of aqueous electrolytes.

TABLE XVI. - SPECIFIC CONDUCTIVITY[55] OF THE SYSTEM NH_4Cl–ICl AT 35°C.

mole % NH_4Cl	0·00	1·34	2·63	5·14	7·51	14·0
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	4·588	6·642	8·558	12·10	15·77	24·18

TABLE XVII. - SPECIFIC CONDUCTIVITY[66] OF THE SYSTEM KCl–ICl AT 35°C.*

mole % KCl	0·00	0·97	2·2	4·3	6·2	8·1	9·9	13·2†	16·7†
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	5·70	9·32	12·4	15·2	17·0	17·0	15·8	15·0	15·0

* Ref. 66 also gives values at 45°C.; ref. 55 has alternative values at 35°C.

† These solutions were saturated and contained the excess potassium chloride in the solid residue.

TABLE XVIII. - SPECIFIC CONDUCTIVITY[61] OF THE SYSTEM KBr–ICl AT 35°C.*

mole % KBr	0·00	0·55	1·95	3·96	7·93	11·28
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	5·39	8·95	15·56	20·50	23·90	21·85

* Ref. 61 also gives values at 45°C.

TABLE XIX. - SPECIFIC CONDUCTIVITY[61] OF THE SYSTEM KI–ICl AT 35°C.*

mole % KI	0·00	1·47	1·67	2·68	3·68	4·95	6·20
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	4·87	12·39	13·87	16·41	18·30	20·24	20·52

* Ref. 61 also gives values at 25° and 45°C.

TABLE XX. - SPECIFIC CONDUCTIVITY[66] OF THE SYSTEM $AlCl_3$–ICl AT 35°C.*

mole % $AlCl_3$	0·00	0·81	1·42	1·79	2·41	5·89	7·28	9·44
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	5·51	5·13	4·73	5·18	5·57	6·70	7·09	7·79
mole % $AlCl_3$	13·22	19·65	24·77	30·80	36·66	45·04	49·08	53·71
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	7·53	5·98	4·71	3·89	3·56	3·20	3·13	3·11

* Ref. 66 also gives values at 45°C.

TABLE XXI. - SPECIFIC CONDUCTIVITY[61] OF THE SYSTEM $AlBr_3$–ICl AT 35°C.* (see also next page)

mole % $AlBr_3$	0·00	2·00	3·97	6·41	8·82	12·27	16·85	20·00
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	5·26	3·85	4·86	5·89	6·64	6·87	6·05	5·78

TABLE XXI (continued)

mole % $AlBr_3$	34·64	39·87	42·40	45·93	46·00	53·23	58·12	68·69
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	2·76	2·12	1·14	1·70	1·00	1·27	0·65	0·37

* Ref. 61 also gives values at 45° and 100°C.

TABLE XXII. - SPECIFIC CONDUCTIVITY[68] OF THE SYSTEM PCl_5–ICl AT 45°C.*

mole % PCl_5	0·00	2·28	4·73	11·66	12·91	14·14
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	5·3	17·2	26·5	25·7	25·3	21·8

* Ref. 68 also gives values at 55°C. Ref. 100 gives $\kappa = 10{\cdot}8 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$ at 0·86 mole % and 50°C.

TABLE XXIII. - SPECIFIC CONDUCTIVITY[64] OF THE SYSTEM PYRIDINE–ICl AT 35°C.*

mole % C_5H_5N	0·00	0·92	2·01	4·42	6·31	8·12	9·86	11·54
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	4·82	10·73	17·14	20·51	21·39	20·20	19·11	17·91
mole % C_5H_5N	16·22	21·74	27·66	28·78	30·85	32·81	34·65	
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	12·34	7·02	4·64	4·26	4·11	3·51	3·37	

* Ref. 64 also gives values at 50°C.

TABLE XXIV. - SPECIFIC CONDUCTIVITY[63] OF THE SYSTEM ACETAMIDE–ICl AT 35°C.*

mole % $AcNH_2$	0·00	2·27	4·60	7·79	14·00	16·94	20·25	23·45	26·70
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	5·17	11·27	16·65	21·81	24·28	23·88	20·89	19·82	17·57
mole % $AcNH_2$	29·39	32·56	37·21	49·06	56·56	60·54	65·38	71·71	76·03
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	17·11	14·38	9·91	4·75	3·18	2·98	2·86	2·75	2·75

* Ref. 63 also gives values at 25° and 45°.

TABLE XXV. - SPECIFIC CONDUCTIVITY[65] OF THE SYSTEM BENZAMIDE–ICl AT 35°C.*

mole % $BzNH_2$	0·00	4·83	9·17	11·88	14·08
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	4·82	21·47	21·70	20·80	17·42
mole % $BzNH_2$	21·17	30·22	33·49	46·28	54·19
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	13·08	5·67	3·62	1·47	0·92

* Ref. 65 also gives values at 50°C.

TABLE XXVI. - SPECIFIC CONDUCTIVITY[73] OF THE SYSTEM *N*-DIETHYLBENZAMIDE–ICl AT 35°C.*

mole % $BzNEt_2$	0·00	4·25	8·07	10·47	12·99	16·81	22·79
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	(4·82)	19·80	22·97	19·40	17·42	14·57	6·30
mole % $BzNEt_2$	28·68	36·05	46·38	52·39	66·95	81·53	
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	3·443	1·959	0·913	0·480	0·400	0·392	

* Ref. 73 also gives values at 50°C.

TABLE XXVII. - SPECIFIC CONDUCTIVITY[75] OF THE SYSTEM THIONYL CHLORIDE–ICl AT 55°C.

mole % $SOCl_2$	0·00	0·18	1·25	2·37	2·66	3·91	4·58	6·10	8·85	14·39
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	4·46	4·01	3·63	3·30	3·19	2·88	2·68	2·36	1·90	1·23

Conductivities which have been measured at a single concentration only are assembled in Table XXVIII. In three instances the conductivity is increased, but with silicon and niobium chlorides the conductivity is diminished at the concentration investigated, suggesting a possible analogy with the behaviour of the aluminium halides (Tables XX and XXI).

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TABLE XXVIII. - SPECIFIC CONDUCTIVITY[75] OF SOLUTIONS IN IODINE MONOCHLORIDE AT 55°C.

Solute	mole %	$\kappa . 10^3$ ohm^{-1} cm^{-1}
Pure solvent	-	4·48
Silicon tetrachloride	0·506	4·02
Niobium pentachloride	0·524	4·28
Titanium tetrachloride	0·513	4·89
Vanadium tetrachloride	0·519	5·04
Antimony pentachloride	0·508	6·20
	0·934	9·25*

* at 50°C.[106]

The density,[63,64,66,73] viscosity[67,73] and phase relations[64,65,66,68] of many of the solutions mentioned in this section have also been investigated, and the results, together with those of electrolysis,[63,64,66,90] ion transport[63,65,66,73,90] and cryoscopy[63,65,68,73,91] of nitrobenzene solutions, have elucidated the structure of the ions and complexes present. The detailed results are too numerous to be covered comprehensively, but the main conclusions reached are outlined in the following paragraphs.

Solutions of potassium chloride in iodine monochloride (Table XVII) contain the addition compound potassium dichloroiodide, which dissociates ionically according to equation (18):-[60,66,90,91,103]

$$KCl + ICl = KICl_2 = K^+ + ICl_2^- \qquad (18).$$

Anhydrous potassium dichloroiodide is a bright orange-yellow compound, m.p. 195°C., which dissociates reversibly into potassium chloride and iodine monochloride at temperatures above 0°C.[60,103]

$$KICl_2\ (s) = KCl\ (s) + ICl\ (g) \qquad (19)$$

The dissociation pressure is as follows:-[60]

t°C.	25	35	40	45	50	55	60
p mm. (±0·05)	0·20	0·40	0·55	0·70	1·00	1·35	1·80

These figures imply a heat of dissociation $\Delta H^\circ_{298 \cdot 16} = 12 \cdot 37$ kg.-cal. mole^{-1}; a free energy of dissociation $\Delta G^\circ_{298 \cdot 16} = 4 \cdot 75$ kg.-cal. mole^{-1}; an entropy of dissociation $\Delta S^\circ_{298 \cdot 16} = 25 \cdot 6$ g.-cal. deg.$^{-1}$ mole^{-1}; and a standard absolute entropy for the complex of $S^\circ_{298 \cdot 16} = 53 \cdot 1$ g.-cal. deg.$^{-1}$ mole^{-1}. When potassium chloride is dissolved in iodine monochloride below 45°C. the compound KCl,2ICl may be obtained as ruby-red crystals, m.p. 45°C.[60] The solubility curves for $KICl_2$ and KCl,2ICl in iodine monochloride intersect at this same temperature which is therefore the transition point for reaction (20). At this temperature the solubility is 6·95 g. KCl/100 g. ICl.[60]

$$KCl,2ICl = KICl_2 + ICl \qquad (20)$$

The density of the solutions at 35° and 45°C. decreases linearly with increasing concentration to a value which is 98·85% of that of the solvent at 8·96 mole-%.[66] The f.p. of the system drops approximately linearly to a eutectic at 12°C. and 12 mole-% of potassium chloride.[66] Electrolysis between platinum electrodes of solutions containing 5-7 mole-% of potassium chloride transports potassium to the cathode where it reacts with the solvent to give potassium chloride and iodine (equation 21).[66] Iodine is also deposited at the cathode as a result of the concurrent electrolysis of the solvent (see

$$K + ICl = KCl + \tfrac{1}{2}I_2 \qquad (21)$$

equation 5). Migration of the ICl_2^- anion, which is furnished by both solvent and solute, increases the concentration of chlorine in the anolyte.[66] Similar results are obtained when various ternary mixtures $KCl-ICl-C_6H_5NO_2$ are electrolyzed between silver electrodes; silver chloride forms on the anode and, in addition, some iodine is deposited (from the ICl_2^- ion).[90] Values for the transport number of the potassium ion in potassium dichloroiodide vary between 0·446 and 0·504; the average value, 0·496, is very close to the transport number of the potassium ion in aqueous potassium chloride.[90] Potassium chloride, which is normally insoluble in nitrobenzene, dissolves in the presence of iodine monochloride, the solubility (and conductivity) increasing with the amount of interhalogen. At the same time, the addition of potassium chloride to a solution of iodine monochloride in nitrobenzene lowers the cryoscopic depression, again indicating complex formation between the two solutes.[91]

Solutions of potassium bromide and potassium iodide have very similar conductive properties to those of potassium chloride (Tables XVII, XVIII, XIX). Although the solutions have not been so extensively investigated, it seems possible that the conductivity is due to the formation of potassium chlorobromoiodide (equation 22) and potassium chlorodi-iodide (equation 23).

$$KBr + ICl = K^+[Br-I-Cl]^- \qquad (22)$$
$$KI + ICl = K^+[I-I-Cl]^- \qquad (23)$$

Solutions of aluminium chloride in iodine monochloride behave somewhat differently (Table XX), for it is the metal atom rather than the iodine which becomes the co-ordination centre of the complex anion (equation 24).[66]

$$AlCl_3 + ICl = I^+[AlCl_4]^- \qquad (24)$$

The density of solutions at 35°, 45° and 65° diminishes approximately in proportion to the concentration of aluminium trichloride and is 86·35% of the density of pure iodine monochloride at 29·13 mole-% solute.[66] Thermal analysis shows eutectics at approx. 14 mole-% (4·5°C.) and at 42·2 mole-% (105°C.), and an unstable addition compound $AlCl_3,2ICl$, m.p. 110°, which is presumably a solvate of the primary complex $IAlCl_4$.[66] Electrolysis of the melt (20 − 30 mole-% $AlCl_3$) liberates iodine at the cathode and aluminium trichloride at the anode. Detailed transference experiments suggest that the transport number of the tetrachloroaluminate ion is somewhere between 0·378 and 0·418.[66] Measurements on nitrobenzene solutions containing iodine monochloride and aluminium trichloride in various ratios lead to similar conclusions, the transference ratio Al/Cl to the anode compartment being close to 1/4 and the transport number of the tetrachloroaluminate anion between 0·205 and 0·318.[90] Cryoscopy of similar solutions in nitrobenzene is somewhat complicated by the relatively low stability of the complex, and it would seem that complexing becomes important only at relatively high concentrations of aluminium trichloride.[91] This may explain the anomalous initial drop in the conductivity curve (Table XX).

Solutions of phosphorus pentachloride in iodine monochloride (Table XXII) contain the addition compound phosphorus iodine hexachloride, $PICl_6$, which has been formulated[68] both as tetrachlorophosphonium dichloroiodide, $PCl_4^+ ICl_2^-$, and as[106] iodine hexachlorophosphate, $I^+PCl_6^-$. (Other reactions in which this compound is formed are discussed under the chemical properties of iodine monochloride, (see page 502)). Thermal analysis between 0 and 40·34 mole-% of phosphorus pentachloride indicates a eutectic at 9·21 mole-% and 9·6°C.[36] The compound $PICl_6$ (50 mole-% of phosphorus pentachloride) sublimes above 200°C. and melts in a sealed tube at 212°−214°C.[108] Evidence for a 1:1 addition compound is also given by the cryoscopic investigation of nitrobenzene solutions containing phosphorus pentachloride and iodine monochloride in varying ratios, the results indicating that each molecule of complex is completely dissociated into two ions.[68] Electrolysis of phosphorus iodine hexachloride in nitrobenzene using a platinum cathode and a silver anode results in cathodic evolution of a gas which renders aqueous silver nitrate turbid (possibly chlorine) and an increase in concentration of phosphorus in the catholyte. At the anode, iodine and silver chloride are deposited.[108] The results confirm that the complex is tetrachlorophosphonium dichloroiodide, $PCl_4^+ICl_2^-$. Other evidence for this structure comes from the spectrophotometry of solutions in acetonitrile ($\lambda_{max.}$ = 341 mμ; cf. $\lambda_{max.}$ (ICl_2^-) = 340 mμ),[109] and from a complete *X*-ray structure determination on the crystals.[110] The space group is $D_{2}^{3}d - P\bar{4}2_1m$ and the unit cell, which contains two molecules, is tetragonal, a = 9·26, c = 5·68 A. The structure consists of tetrahedral PCl_4^+ ions and linear $Cl-I-Cl^-$ ions, and the *X*-ray density of the crystals is 2·53 g. ml.$^{-1}$ The complex is soluble in iodine monobromide and in bromine to give conducting solutions; e.g. at 45°C. pure bromine has $\kappa < 10^{-8}$ ohm^{-1} cm.$^{-1}$, a solution containg 1·0 mole-% $PICl_6$ in bromine has κ = 4·5 × 10^{-6} ohm^{-1} cm.$^{-1}$, and a solution containing 10 mole-% has κ = 2·0 × 10^{-2} ohm^{-1} cm.$^{-1}$.[68] The solubility of tetrachlorophosphonium dichloroiodide in several solvents at 20°C. and the electrical conductivity of the saturated solution are given in Table XXIX. The compound is hydrolysed by water or aqueous ethanol[108] and is completely dissociated into its constituent molecules PCl_5 and ICl in carbon tetrachloride.[109]

TABLE XXIX. - SOLUBILITY AND CONDUCTIVITY OF $PICl_6$ IN NON-AQUEOUS SOLVENTS AT 20°C.[68,108]

Solvent*	Solubility (wt. %)	κ,ohm^{-1} cm.$^{-1}$
acetonitrile	10·1	7·7 × 10^{-3}
nitrobenzene	2·6	1·3 × 10^{-3}
ethyl bromide	1·0	3·8 × 10^{-5}
chloroform	1·2	1·1 × 10^{-5}
dioxan	1·5	<1 × 10^{-6}

* The following solvents dissolve <0·5 wt. % $PICl_6$ and the saturated solutions are non-conductors ($\kappa < 10^{-8}$ ohm^{-1} cm.$^{-1}$):- carbon disulphide, carbon tetrachloride, methyl iodide, ethyl iodide, ethyl ether, benzene, toluene, xylene, bromobenzene.

Solutions of pyridine in iodine monochloride have a conductivity higher than that of the pure interhalogen because of the stabilizing influence of the donor molecule on the iodine cation (Table XXIII). Thermal analysis of the system reveals two compounds C_5H_5N,ICl m.p. 128·5°C. and $C_5H_5N,2ICl$ m.p. 35·1°C., and three eutectics: 20·73 mole-% C_5H_5N (–6·3°C.), 35·1 mole-% C_5H_5N (23·6°C.), and 98·9 mole-% C_5H_5N (–50·2°C.).[64] The m.p. of recrystallized pyridine-iodine monochloride is[34] 134°C. The density of the system at 50°C. falls from 3·166 for pure ICl to 2·332 for a solution containing 37·24 mole-% of pyridine. Electrolysis points to ionic dissociation of the melt according to equations (25) and (26).[67]

$$C_5H_5N,ICl \rightleftharpoons C_5H_5NI^+ + Cl^- \qquad (25)$$

$$C_5H_5N,2ICl \rightleftharpoons C_5H_5NI^+ + ICl_2^- \qquad (26)$$

Equation (26) should be compared with equation (5) for the self-ionization of iodine monochloride.

Solutions of acetamide in iodine monochloride (Table XXIV) and of mixtures of acetamide and iodine monochloride in nitrobenzene, have been studied by means of thermal analysis, conductivity, viscosity, density, electrolysis, ion transport, solubility and cryoscopy.[63,67] The compounds formed are

$CH_3{\cdot}CONH_2,ICl$ and $(CH_3{\cdot}CONH_2)_2,ICl$, and the probable ionization schemes are given in equations (27) and (28).

$$CH_3{\cdot}CONH_2,ICl = CH_3{\cdot}CONH_2,I^+ + Cl^- \qquad (27)$$
$$(CH_3{\cdot}CONH_2)_2,ICl = (CH_3{\cdot}CONH_2)_2I^+ + Cl^- \qquad (28)$$

The conductivity,[63,67] viscosity[63,67] and density[63] of the molten 1:1 compound at 25°, 35° and 45°C. are $\kappa_{25} = 2{\cdot}5 \times 10^{-3}$, $\kappa_{35} = 4{\cdot}5 \times 10^{-3}$, $\kappa_{45} = 6{\cdot}7 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$; $\eta_{25} = 39{\cdot}40$, $\eta_{35} = 22{\cdot}04$, $\eta_{45} = 13{\cdot}15$ cp.; $d_4^{35} = 2{\cdot}157$. Corresponding values for the 2:1 compound are $\kappa_{25} = 1{\cdot}56 \times 10^{-3}$, $\kappa_{35} = 2{\cdot}83 \times 10^{-3}$, $\kappa_{45} = 4{\cdot}69 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$; $\eta_{25} = 60{\cdot}27$, $\eta_{35} = 29{\cdot}95$; $\eta_{45} = 17{\cdot}48$ cp.; $d_4^{35} = 1{\cdot}794$.

Similar measurements on the system benzamide–iodine monochloride (Table XXV) have established a 1:1 compound $C_6H_5{\cdot}CONH_2,ICl$, m.p. 36·9° (eutectics at 11 mole-% $BzNH_2$ (−23°) and 53·2 mole-% $BzNH_2$ (+23·5°C.).[65,67] The density curve for the system at 50°C. is somewhat convex to the composition axis and falls to 55% of the value for the pure solvent at 58 mole-% $BzNH_2$. The density of the compound benzamide–iodine monochloride itself is $d_4^{50} = 1{\cdot}850$[65] and hence its molar conductivity is 0·184 ohm^{-1} cm.^{2} The viscosity at 50°C. is 23·07 centipoises.[67] Ion-transference experiments are consistent with the presence of both a monomer and a dimer which ionize as shown in equations (29) and (30).

$$C_6H_5{\cdot}CONH_2,ICl = C_6H_5{\cdot}CONH_2,I^+ + Cl^- \qquad (29)$$
$$(C_6H_5{\cdot}CONH_2,ICl)_2 = (C_6H_5{\cdot}CONH_2)_2I^+ + ICl_2^- \qquad (30)$$

There appears to be a dynamic stepwise dissociation of the dimeric cation according to equation (31).[65]

$$(C_6H_5{\cdot}CONH_2)_2I^+ = C_6H_5{\cdot}CONH_2 + C_6H_5{\cdot}CONH_2,I^+ = 2C_6H_5{\cdot}CONH_2 + I^+ \qquad (31)$$

Diethylbenzamide (Table XXVI) dissolves in iodine monochloride with the liberation of much heat.[73] The density of the conducting solution at 35° diminishes regularly (but not linearly) from 3·192 for pure iodine monochloride to 1·071 for pure diethylbenzamide. The viscosity curve, on the other hand, has a well-defined maximum at 50 mole-%. The properties of the 1:1 addition compound diethylbenzamide–iodine monochloride in the molten state are:[69] $d_4^{35} = 1{\cdot}681$, $d_4^{50} = 1{\cdot}602$; $\eta_{35} = 54{\cdot}5$, $\eta_{50} = 18{\cdot}5$ cp.; $\kappa_{35} = 0{\cdot}47 \times 10^{-3}$, $\kappa_{50} = 0{\cdot}98 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$ These figures correspond to a molar conductivity of 0·21 at 50° which is quite appreciable when the high viscosity is considered. Investigations of nitrobenzene solutions of mixtures of diethylbenzamide and iodine monochloride by means of conductivity, ion transference and cryoscopy have shown that the simple complex ionizes in accord with equation (32) and also that there is some dimerization to a complex which ionizes as shown in equation (33).[73]

$$C_6H_5{\cdot}CONEt_2,ICl = C_6H_5{\cdot}CONEt_2I^+ + Cl^- \qquad (32)$$
$$(C_6H_5{\cdot}CONEt_2,ICl)_2 = (C_6H_5{\cdot}CONEt_2)_2I^+ + ICl_2^- \qquad (33)$$

Similar work on nitrobenzene solutions of acetanilide and iodine monochloride are interpreted in terms of a 1:2 complex, acetanilide–di(iodine monochloride), which presumably has the structure $[CH_3{\cdot}CONHC_6H_5I]^+[ICl_2]^-$.[73]

It will be observed that, in nearly all the solutions discussed, the solute reacts with iodine monochloride to furnish either the iodine cation (e.g. equations 24 and 25), or the dichloroiodide anion (e.g. equation 18), or both (e.g. equation 26). As the pure solvent, iodine monochloride, dissociates to give these same two ions (equation 5) it is possible to set up a solvent acid-base scheme.[2] Those complexes which ionize to give the characteristic cation of the solvent (I^+) are solvo-acids, and those complexes which furnish the characteristic anion (ICl_2^-) are solvo-bases (cf. H^+ and OH^- in water).[75,106,107] Donors like pyridine which may furnish both I^+ and ICl_2^- in solution are best considered as reagents which enhance the self-ionization of the solvent by means of co-ordination. Neutralization reactions may be carried out between solvo-acids and solvo-bases, and the end-points detected electrometrically. Thus, when dissolved in iodine monochloride, the solvo-acid iodine hexachloroantimonate (*i.e.* $SbCl_5,ICl$) may be neutralized by the solvo-base potassium dichloroiodide to form a salt, potassium hexachloroantimonate:-[75,106]

$$I^+SbCl_6^- + K^+ICl_2^- = K^+SbCl_6^- + 2ICl \qquad (34)$$

Similarly, tin tetrachloride may be thought of as generating a dibasic acid ($SnCl_4,2ICl = I_2SnCl_6$) which may be titrated with a solution of potassium chloride in iodine monochloride to give potassium hexachlorostannate.[75,106]

$$2KICl_2 + SnCl_4 = K_2SnCl_6 + 2ICl \qquad (35)$$

Further examples of chemical reactions in iodine monochloride are discussed in the next sub-section, but it is convenient to summarize here the various compounds which are known to dissolve in this solvent to give solvo-acidic and solvo-basic solutions respectively. This is done in Table XXX. It may also be noted that the use of iodine monochloride as a preparative medium in inorganic chemistry is restricted both by the extent of solvolysis, which prevents the isolation of many compounds, and by the frequent necessity to isolate reaction products by extraction techniques rather than by precipitation.[107]

TABLE XXX. - SOLVO-ACIDS AND -BASES IN IODINE MONOCHLORIDE*

Solvo-acids	Solvo-bases
$AlCl_3,ICl = I^+AlCl_4^-$	$KCl,ICl = K^+ICl_2^-$
$SbCl_5,ICl = I^+SbCl_6^-$	$RbCl,ICl = Rb^+ICl_2^-$
$TiCl_4,2ICl = (I_2TiCl_6)$	$CsCl,ICl = Cs^+ICl_2^-$
$SnCl_4,2ICl = (I_2SnCl_6)$	$NH_4Cl,ICl = NH_4^+ICl_2^-$
$VCl_4,2ICl = (I_2VCl_6)$	†$PCl_5,ICl = PCl_4^+ICl_2^-$
$NbCl_5,ICl = (INbCl_6)$	

* The complexes in parentheses are postulated hypothetically to explain the observed reactions. They are too highly decomposed by solvolysis to be isolated as stable complexes.

† The claim that this complex is amphoteric and may react as the solvo-acid $I^+PCl_6^-$ does not seem to have been confirmed.[75,106]

CHEMICAL PROPERTIES OF IODINE MONOCHLORIDE

Iodine monochloride is a very reactive compound which quickly attacks the eyes, nose and throat and causes bad skin burns. The most effective antidote for burns is 6 N-hydrochloric acid.[55] It also reacts vigorously with cork, rubber and other organic substances. The chemical properties of iodine monochloride may be conveniently discussed under six fairly distinct headings: reactions with elements; reactions with inorganic compounds; reactions with organic compounds; molecular addition compounds; addition reactions with unsaturated organic compounds; and applications to analysis.

The reaction of iodine monochloride with about forty elements has been studied.[111] If reaction occurs it is invariably chlorination, never iodination. Chlorination frequently goes to the highest valency state and is complete if the chloride is insoluble in iodine monochloride. The excess iodine monochloride and the liberated iodine may be extracted with carbon tetrachloride to give the reaction product. In exceptional cases a lower chloride is formed, e.g. vanadium trichloride from metallic vanadium.[112] This is a most useful method of preparing anhydrous vanadium trichloride which is otherwise difficult to obtain. Other useful preparative reactions are the 100% yields of gold trichloride, mercury dichloride and tellurium tetrachloride, which are obtained by warming the metals with the interhalogen. Reaction with sodium is incomplete because of a protective layer of sodium chloride. By contrast, potassium reacts explosively to give potassium dichloroiodide. No reaction is observed with boron, carbon, silicon, lead, cadmium, zirconium, niobium, tantalum, chromium, molybdenum, tungsten or platinum under the conditions employed.[111] The results are summarized in Table XXXI.

TABLE XXXI - REACTION OF ELEMENTS WITH IODINE MONOCHLORIDE[111]

Element	Product	% Yield	Element	Product	% Yield
Na	NaCl	5	Cu	$CuCl_2$	45
K	$KICl_2$	100	Ag	AgCl	55
Mg	$MgCl_2$	5	Au	$AuCl_3$	100
Ca	$CaCl_2$	30	Zn	$ZnCl_2$	50
Ba	$BaCl_2$	55	Cd	none	-
B	none	-	Hg	$HgCl_2$	100
Al	$AlCl_3$	100	Ti	$TiCl_4$	100
In	$InCl_3$(?)	1	Zr	none	-
C	none	-	V	VCl_3	100
Si	none	-	Nb	none	-
Ge	$GeCl_4$(?)	100	Ta	none	-
Sn	$SnCl_4$	100			
Pb	none	-	Cr	none	-
			Mo	none	-
P_{red}	PCl_5	100	W	none	-
P_{white}	PCl_5	55	Mn	$MnCl_2$	10
As	$AsCl_3$	100			
Sb	$SbCl_5$	100	Fe	$FeCl_2+FeCl_3$	65
Bi	$BiCl_3$	60	Co	$CoCl_2$	25
S	S_2Cl_2(?)	100	Ni	$NiCl_2$	7
Se	$SeCl_4$(?)	100	Pt	none	-
Te	$TeCl_4$	100			

The mechanism of the photochemical reaction between gaseous iodine monochloride and hydrogen has been the subject of some controversy.[69,113-118] From experiments in a flow system with p_{ICl} = 40 mm. and p_{H_2} = 715 mm. it now seems that the quantum yield of hydrogen chloride is 1·5 ± 0·2, although this value may be high.[118] When the reaction is studied in a static system at several pressure ratios using an exciting radiation of 4358 A., the quantum yield increases from 0 to 0·037 when the pressure ratio p_{H_2}/p_{ICl} increases from 0 to 20.[69] The nature of the surface is important, a coating of sodium chloride on the glass increasing the yield 6-fold. The results in both flow and static systems appear to be consistent with the following mechanism:-[69,118]

$$\begin{array}{lrr} & \Delta H & E_{\text{act.}} \\ & \multicolumn{2}{c}{\text{kg.-cal. mole}^{-1}} \\ (a)\ ICl + h\nu = I + Cl & & \\ (b)\ Cl + H_2 = HCl + H & 0{\cdot}9 & 6{\cdot}5 \\ (c)\ H + ICl = HCl + I & -52{\cdot}2 & 2{\cdot}7 \\ (d)\ Cl + ICl = Cl_2 + I & -7{\cdot}5 & 2{\cdot}7 \\ (e)\ I + I + M = I_2 + M & -35{\cdot}4 & - \end{array}$$

If only reactions (*a*), (*b*), (*c*) and (*e*) were involved, then the quantum yield of hydrogen chloride would be exactly 2. The lower values obtained suggest that both hydrogen and iodine monochloride compete for the atomic chlorine according to reactions (*b*) and (*d*).[118] The homogeneous, thermal, dark reaction between iodine monochloride and hydrogen has also been studied both experimentally[119] and theoretically.[120,121] The rate of reaction becomes appreciable above 200°C. and the rate constants k_t at t°C. are $k_{205} = 0{\cdot}031 \pm 0{\cdot}006$; $k_{230} = 0{\cdot}17 \pm 0{\cdot}06$; and $k_{240} = 0{\cdot}35 \pm 0{\cdot}06$. The corresponding activation energy is 33·9 kg.-cal. mole^{-1}.

Iodine monochloride is not appreciably hygroscopic in bulk but on prolonged exposure to a moist atmosphere it forms a surface film of iodine pentoxide.[85] The compound is hydrolysed by pure water according to equations (10) and (11) unless it is stabilized by hydrochloric acid or sodium chloride.[47,53,59,85,86,122] Metal oxides react to give only chlorides, and not mixtures of chlorides and iodides as previously thought.[75] On the other hand, silver sulphide and the sulphides of zinc, cadmium and lead (II) react vigorously to give the corresponding iodide and disulphur dichloride:-[104]

$$2MS + 4ICl = 2MI_2 + S_2Cl_2 + Cl_2 \qquad (36)$$

The nitrates, sulphates and cyanides of sodium and potassium are converted into chlorides with the concurrent formation of iodine nitrate, sulphate and cyanide.[104] Other cyanides which react according to equation (37) are those for which M is ammonium, cæsium, cadmium, copper (I), silver and lead (II):-[104]

$$MCN + ICl = MCl + ICN \qquad (37)$$

Potassium cyanate forms potassium chloride and iodine tricyanate (equation 38) and a similar reaction is given by lead (II) cyanate.

$$3KCNO + 3ICl = 3KCl + I(CNO)_3 + I_2 \qquad (38)$$

The analogous reaction (39) with thiocyanates to give iodine trithiocyanate occurs when M is ammonium, potassium, silver or lead (II).

$$3MCNS + 3ICl = 3MCl + I(CNS)_3 + I_2 \qquad (39)$$

Iodine tricyanate is a dark brown powder which chars without melting at temperatures above 160°C.; it is sparingly soluble in water and ethanol. Iodine trithiocyanate is a yellow-brown powder which chars above 260°C.; it dissolves in concentrated sulphuric acid but is sparingly soluble in water and most organic solvents.[104] In acetic acid solution, potassium cyanide and thiocyanate react as above but the cyanate decomposes. The heavy metal acetates give yellow, crystalline, intermediate products of composition $Pb_2(OAc)_2,ICl$ and $Cd_3(OAc)_2,2ICl$ which may speculatively be considered as basic salts in the acetic acid solvent system: $PbICl,Pb(OAc)_2$; and $2CdICl, Cd(OAc)_2$ or $CdCl_2,CdI_2,Cd(OAc)_2$. The corresponding copper salt $Cu_2(OAc)_2$, ICl is pale blue and may hypothetically be formulated[104] as $CuICl,Cu(OAc)_2$. Phosphorus trichloride undergoes an intensely exothermal reaction with iodine monochloride but the anticipated product in which one chlorine atom of the pentachloride is replaced by iodine, PCl_4I, is not obtained. In the first stage of the reaction the trichloride is oxidized by the interhalogen to the pentachloride and this then reacts to form the addition compound phosphorus iodine hexachloride[74] (see page 497).

$$PCl_3 + 2ICl \rightleftharpoons PCl_5 + I_2 \qquad (40)$$
$$PCl_5 + ICl = PICl_6 \qquad (41)$$

As reaction (40) is a balanced equilibrium, the final product may also be obtained by the reaction of phosphorus pentachloride with iodine. A fourth preparation of phosphorus iodine hexachloride is by the addition of iodine trichloride to phosphorus trichloride.[74,108]

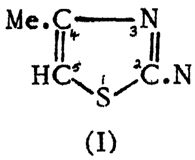
The reaction of iodine monochloride with organic compounds may result in complete decomposition, iodination, chlorination or the formation of an addition compound. Formic acid, in the presence of aqueous hydrochloric acid, undergoes a second order reaction to give iodine, hydrogen chloride and carbon dioxide.[123]

$$\begin{array}{ll} ICl + HCO_2H = HI + HCl + CO_2 & \text{(slow)} \\ ICl + HI = I_2 + HCl & \text{(fast)} \\ \hline 2ICl + HCO_2H = I_2 + 2HCl + CO_2 & \end{array} \qquad (42)$$

The reaction rate decreases with increasing concentration of hydrochloric acid and is $4{\cdot}7 \times 10^{-5}$ l. mole^{-1} min.$^{-1}$ at 45°C. When formamide is used instead of formic acid, ammonium chloride is also formed:-[123]

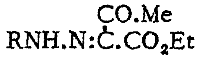
$$2ICl + HCONH_2 + H_2O = I_2 + HCl + NH_4Cl + CO_2 \qquad (43).$$

Acetanilide and other N- or ring-substituted anilines are iodinated in acetic acid,[45] as are Schiff's bases when dissolved in glacial acetic acid, carbon tetrachloride or chloroform.[124] Salicylic acid, o-HO.C_6H_4.CO_2H, in glacial acetic acid gives 2-hydroxy-3,5-di-iodobenzoic acid in 92% yield, and 4-hydroxybenzoic acid yields 84% of the 3,5-di-iodo derivative.[54] Tyrosine, p-HO.C_6H_4.$CH_2CH(NH_2)$.CO_2H, reacts with iodine monochloride in acetic acid to give 85% of the di-iodo derivative.[125] The interhalogen, when dissolved in 6 N-hydrochloric acid solution, gives the mono-(5-) or di-iodo-(5,7-) derivatives of 8-hydroxyquinoline and 8-aminoquinoline, depending on the number of moles of iodine monochloride added.[48] If the same reaction is carried out in chloroform solution, molecular addition compounds may be isolated as stable intermediates (see Table XXXII). Various substituted thiazoles may also be iodinated in hydrochloric acid solution to give the 5-iodo derivative, e.g. 2-amino-4-methylthiazole, (I), 2-aminothiazole, 2-amino-4-thiazolecarboxylic acid, 2-acetamidothiazole, 2-acetamido-4-methylthiazole, and 2-acetamido-4-thiazolecarboxylic acid.[126] These compounds are useful as narcotics. Occasionally, thiazole–iodine monochloride addition compounds are formed (see Table XXXII). A solution of iodine monochloride in acetic acid iodinates phenols, hydroxybenzoic acids, hydroxynaphthoic acids and aromatic ethers.[46] Under different conditions, the same reagent chlorinates hydroxynaphthoic acids, alizarin and di(p-hydroxyphenyl), the latter compound yielding the 3,3′,5,5′-tetrachloro derivative.[127] Iodine monochloride reacts with 1,4-dioxan to give the 2,3-dichloro derivative[128] (see also Table XXXII). Similarly, N-substituted malonamides, which contain an active methylene group, usually give the corresponding dichloromalonamide, but in some instances only one of the active hydrogens is replaced, a second chlorine entering the ring, e.g. N-phenylmalonamide, PhNH.CO.CH_2.CO.NH_2, yields (chloromalono)(chlorophenyl)amide, ClC_6H_4.NH.CO.CHCl.CO.NH_2.[129] Iodine monochloride reacts with organo-mercury compounds in various solvents to give iodides except when secondary reaction with excess interhalogen converts the organic iodide into a chloride.[130] Thus, 95% yields of p-iodoanisole, p-MeO.C_6H_4I, are obtained from both di(p-anisyl)mercury, $(p\text{-MeO.}C_6H_4)_2Hg$, and p-anisylmercuric chloride, $(p\text{-MeO.}C_6H_4)HgCl$, and β-naphthylmercuric chloride, $(\beta\text{-}C_{10}H_7)HgCl$, gives β-iodonaphthalene in similar yield. The same reaction, but in lower yield, is given by diphenylmercury and by p-tolylmercuric chloride, p-MeC_6H_4HgCl. On the other hand, (β-phenylethyl)-mercuric chloride, $PhCH_2.CH_2HgCl$, gives about equal amounts of the chloride and the iodide.[130] The action of iodine monochloride on arylazoacetoacetates,

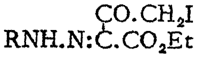


(I)

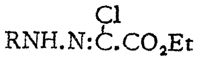
(II), in acetic acid is considerably influenced, or sometimes completely altered, by the nature of the groups present in the phenyl nucleus.[131]


$\text{RNH.N:}\overset{\text{CO.Me}}{\text{C}}\text{.CO}_2\text{Et}$

(II)

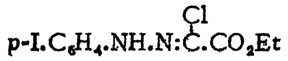

$\text{RNH.N:}\overset{\text{CO.CH}_2\text{I}}{\text{C}}\text{.CO}_2\text{Et}$

(III)

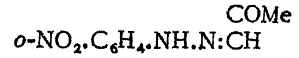

$\text{RNH.N:}\overset{\text{Cl}}{\text{C}}\text{.CO}_2\text{Et}$

(IV)

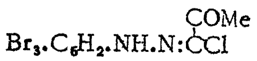
When R is 2,4,6-tribromo, 2,4-dibromo, p-bromo-, p-nitro-, or *o*-nitro-phenyl, then iodine is substituted in the acetyl group, (III) (80% yield). When R is 2,4-dinitrophenyl, then chlorine substitution in the acetyl group occurs (70% yield); but when R is p-chlorophenyl, the acetyl group is replaced by chlorine, (IV), (20% yield). When R is phenyl, the acetyl group is replaced by chlorine and iodine substitutes *para* in the phenyl nucleus, (V), (20% yield).[131]


$\text{p-I.C}_6\text{H}_4\text{.NH.N:}\overset{\text{Cl}}{\text{C}}\text{.CO}_2\text{Et}$

(V)


$o\text{-NO}_2\text{.C}_6\text{H}_4\text{.NH.N:}\overset{\text{COMe}}{\text{CH}}$

(VI)


$\text{Br}_3\text{.C}_6\text{H}_2\text{.NH.N:}\overset{\text{COMe}}{\text{C}}\text{Cl}$

(VII)

The related compound pyruvic aldehyde-*o*-nitrophenylhydrazone, (VI), is monoiodinated in good yield in the methyl group, but pyruvic aldehyde-tribromophenylhydrazone is chlorinated at the aldehyde position to give compound (VII) in 20% yield.[131]

The kinetics of exchange reactions between iodine monochloride and benzyl bromide or iodide in dilute carbon tetrachloride at 25° are second order with respect to the interhalogen and first order with respect to the organic halide.[133] If X = I or Br, then the rate of reaction is $d[IX]/dt = k[PhCH_2X][ICl]^2$. The proposed mechanism proceeds through the formation of a complex, $PhCH_2X.ICl$, followed by a rate-determining Walden-inversion reaction between the complex and a further molecule of interhalogen to give the products, viz. benzyl chloride, iodine and regenerated iodine monochloride.[133] The exchange mechanism with *iso*propyliodide is also second order with respect to iodine monochloride, but the reaction rate is not proportional to the concentration of organic iodide because a large fraction of this is complexed to give Me_2CHI, ICl, $K \simeq 7{\cdot}4$ l. $mole^{-1}$. In this instance, details of the reaction mechanism remain obscure.[133] The kinetics of halogen substitution reactions between iodine monochloride and aromatic compounds of the type anisole, acetanilide, pentamethylbenzene and p-tolyl methyl ether satisfy a third-order equation.[97] In acetic acid and in chlorobenzene solutions, the iodination of these compounds is accompanied by some chlorination, the relative degree of chlorination being modified either by the removal of hydrogen chloride as it is formed, or by change of solvent.[97] The variation in the type of substitution is related to the molecular constitution of the interhalogen in the various solvents (see page 489 where the dual character of iodine monochloride in solutions is discussed in relation to electrical conductivity and absorption spectra). Thus, iodine monochloride in carbon tetrachloride reacts but slowly with silver perchlorate to precipitate silver chloride, whereas in nitrobenzene, in which the interhalogen is ionized, precipitation is immediate.[98] Another example of the variation in chemical reactivity of iodine monochloride as a function of the properties of the solvent is its reaction with salicylic acid. The main reaction between solid salicylic acid and gaseous iodine monochloride is chlorination, for homolytic fission of the interhalogen leads to chlorination by chlorine rather than iodination by iodine.[98] However, in carbon tetrachloride solution (low dielectric constant) iodination predominates, accompanied to a small extent by chlorination; in such a solution, and in the presence of a phenolic group, heterolytic fission is induced in addition to the normal thermal dissociation so that both iodination by the iodine cation and chlorination by chlorine molecules occurs. Finally, in a solvent of high dielectric constant such as nitrobenzene, heterolytic fission is always favoured, and iodination by I^+ is observed exclusively.[98]

The molecular addition compounds of iodine monochloride with organic compounds are summarized in Table XXXII. Adducts with inorganic compounds, and certain unstable addition complexes with organic compounds have already been discussed (see pages 490–492, 500 and 496–498). The compounds listed in Table XXXII are prepared by direct interaction of the components either in acid media (acetic acid or 6 N-hydrochloric acid) or in an inert solvent such as carbon tetrachloride or chloroform. The compounds are frequently pale yellow, suggesting the presence of the dichloroiodide ion. The complex with dioxan is red-brown[134] and those with the hydrochlorides of p-phenanthroline dihydrate and 6-aminoquinoline are orange-red.[48] The 1:1:1 complexes formed between an organic donor, hydrogen chloride, and iodine monochloride are presumably salts of quaternary nitrogen cations and the dichloroiodide anion, e.g. $C_5H_5N,HCl,ICl = C_5H_5NH^+ICl_2^-$.

TABLE XXXII.- MOLECULAR ADDITION COMPOUNDS OF IODINE MONOCHLORIDE

Donor	mole ratio donor : ICl	m.p. °C.	refs.
Dioxan	1:1	56–58	134
Pyridine	1:1	134,135	34,48
	1:2	35·1	64
Pyridine, HCl	1:1	182	48
Quinoline	1:1	157	48
Quinoline, HCl	1:1	118	48
*iso*Quinoline	1:1	158	48
*iso*Quinoline, HCl	1.1	155	48
8-Hydroxyquinoline	1:1	182–184	135
	1.2	182	135
6-Hydroxyquinoline	1:1	252	48
5-Aminoquinoline	1:1	198	48
6-Aminoquinoline, HCl	1:1	206	48
Acridine, HCl	1:1	220	48
o-Phenanthroline, HCl	1:1	167	48
p-Phenanthroline, HCl, $2H_2O$	1:1	197	48
2-Acetylamino-4-methyl-5-iodothiazole	2:1	148	126,136
2-Amino-5-iodo-4-thiazolecarboxylic acid	2:1	217–218	126
Benzamide	1:1	36·9	65
N-Diethylbenzamide	1:1	?	73
Acetamide	1:1	?	63,67
	2:1	?	67
Triphenylmethyl bromide	1:2	?	133

Iodine monochloride readily adds on to olefinic double bonds, the reaction being initiated by the iodine end of the interhalogen.[137,138] In hydrochloric acid solution, propylene yields 69% of the 2-chloro-1-iodo-derivative, MeCHCl. CH_2I, and 31% of the 1-chloro-2-iodo-derivative, MeCHI.CH_2Cl; styrene yields 95% of 1-phenyl-1-chloro-2-iodoethane, Ph.CHCl.CH_2I; and ethylenesulphonic acid, CH_2:CH.SO_3H, yields 90% of 2-chloro-1-iodoethyl-1-sulphonic acid, $ClCH_2$.CHI.SO_3H. A similar reaction with crotonic acid, MeCH:CHCO_2H, yields 92% of β-chloro-α-iodobutyric acid, MeCHCl.CHI.CO_2H, but if the interhalogen is dissolved in chloroform and the reaction is conducted in boiling pyridine, then α-iodocrotonic acid is obtained by substitution.[137] Butadiene in methylene chloride at −35°C. gives mainly the 1,4-addition product, $\mathrm{ICH_2.CH{:}CH.CH_2Cl}$, accompanied by 22% of the 1,2-product, $\mathrm{ICH_2.CHCl.CH{:}CH_2}$.[138] The reaction has been used to determine the degree of unsaturation in natural and synthetic rubbers,[139-141] and some attempt has been made to elucidate its mechanism.[38,142,143] Thus, in acetic acid solution, the addition of iodine monochloride to unsaturated fatty acids shows third-order kinetics; it is 33 times faster than the addition of iodine bromide, but 40 times slower than the addition of bromine monochloride.[38]

Iodine monochloride finds several uses in volumetric analysis. A solution of the interhalogen in dilute hydrochloric acid cannot be titrated directly with sodium thiosulphate, but if sodium acetate and potassium cyanide are added first, the reaction is rapid and quantitative.[42]

$$\begin{array}{l} \mathrm{ICl + CN^- = ICN + Cl^-} \\ \underline{\mathrm{ICN + 2S_2O_3^{2-} = I^- + CN^- + S_4O_6^{2-}}} \\ \mathrm{ICl + 2S_2O_3^{2-} = I^- + Cl^- + S_4O_6^{2-}} \qquad (44) \end{array}$$

Arsenious oxide may be titrated to the starch end-point in bicarbonate solution.[144]

$$\mathrm{H_2AsO_3^- + ICl + 2HCO_3^- = H_2AsO_4^- + I^- + Cl^- + H_2O + 2CO_2} \qquad (45)$$

At the end-point, iodine is liberated according to equation (46):-

$$\mathrm{ICl + I^- = I_2 + Cl^-} \qquad (46).$$

Phenol, resorcinol, 2-naphthol and 8-hydroxyquinoline may be directly titrated with iodine monochloride in 4 N-hydrochloric acid using the starch-iodide indicator.[145] Iodine monochloride itself may serve as a convenient indicator in reactions other than the Andrew's titration with iodates. Iodide may be directly titrated to the iodine monochloride end-point with potassium permanganate, potassium dichromate, potassium iodate or ceric sulphate solutions.[146] Advantages of this procedure are that arsenic and antimony may be determined directly with potassium permanganate or ceric sulphate; the electrometric end-point for ceric titrations is avoided; the danger of losing iodine when iodates are used is eliminated; and it is possible to standardize several oxidizing agents against the same primary standard.[50,147] In the same way, thallous salts may be precisely determined with 0·1 N-iodate solution in 1−5 N-hydrochloric acid using the iodine monochloride end-point.[148]

IODINE TRICHLORIDE

Iodine trichloride may be prepared by passing chlorine over iodine until it is converted into the monochloride and then volatilizing the monochloride at a higher temperature into the stream of chlorine. The product is condensed at 0°C. and may be sealed off under reduced pressure. The process, although rapid, depends critically on the dimensions of the apparatus and the flow-rate of chlorine.[149] Further disadvantages are the low yield and a slight contamination of the product with iodine monochloride. The trichloride is most conveniently prepared by condensing chlorine from a commercial cylinder into a large test-tube or flask cooled in solid carbon dioxide/ether, and then adding finely powdered iodine to fill the liquid space. Excess chlorine is removed by vaporization into a second flask where the process may be repeated. The yield is 100% based on the iodine used.[150]

PHYSICAL PROPERTIES OF IODINE TRICHLORIDE

X-Ray analysis of the crystal structure of iodine trichloride has revealed that the compound consists of planar molecules, $\mathrm{I_2Cl_6}$, having negligible deviations from the point-group symmetry mmm.[151] Fig. 2 shows that each iodine atom is surrounded by two chlorine atoms at 2·38 and 2·39 A. and two others at 2·68 and 2·72 A. It will be noted that all these values are considerably greater than the I–Cl bond distance in iodine monochloride, 2·32 A. The Cl–Cl distances within the molecule (3·51, 3·56, 3·61 and 3·67 A.) are very similar to the closest approach of two chlorine atoms in different molecules (3·55, 3·57 and 3·60 A.).

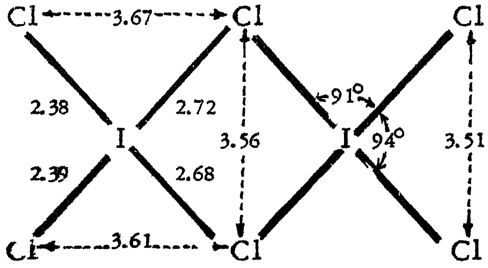


Figure 2.

The triclinic crystals are complexly twinned and belong to the space group P$\bar{1}$ (no piezoelectric effect). There is one molecule of di-iodine hexachloride per unit cell:-

a = 5·71 ± 0·03   α = 130°50′ ± 10′
b = 10·88 ± 0·02   β = 80°51′ ± 1°
c = 5·48 ± 0·03   γ = 108°30′ ± 10′

The b-axis corresponds with the I–I vector and is the needle axis of the crystal. The calculated density,[151] 3·17 ± 0·06 g. ml.$^{-1}$, agrees with an experimental value d^{-40} = 3·203 g. ml.$^{-1}$ which was obtained pyknometrically using liquid chlorine as the confining fluid.[72] The molar volume (I_2Cl_6) is 147·2 ml.[151] or 145·7 ml.[72]

The electrical conductivity of solid iodine trichloride increases from 1·90 × 10^{-5} ohm^{-1} cm.$^{-1}$ at 70·0°C. to 8·35 × 10^{-3} ohm^{-1} cm.$^{-1}$ just below the m.p.[70] The results, which were obtained by fusing the trichloride under pressure and then solidifying it in a conductivity cell with tungsten electrodes, are presented in Table XXXIII. There is a slight discontinuity as the compound melts. The conductivity of the liquid increases slowly to a maximum of 9·6 × 10^{-3} ohm^{-1} cm.$^{-1}$ at 111°C. after which it decreases until, at 145°C., it is equal to that of the solid ten degrees below the m.p. (Table XXXIV).[70] The absence of a decomposition potential in the melt, and the approximate continuity of the conductivity through the m.p., might seem to argue against an ionic conduction mechanism, but the facts are also difficult to interpret on a semiconduction mechanism. Further work on transport experiments and on the thermoelectric effect has been advocated to elucidate the type of conduction occurring.[70] The X-ray structure of the solid indicates that there are two distinct I–Cl bond distances and this might be interpreted in terms of an ionic form $ICl_2^+ICl_4^-$, but the structure factors involved show that the effect is more complicated than a simple mesomerism between the two forms[151] shown in Fig. 3.

TABLE XXXIII.- SPECIFIC CONDUCTIVITY OF SOLID IODINE TRICHLORIDE[70]

t°C.	70·0	79·0	84·8	89·9	95·0	96·2	97·7	99·4	100·1
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	0·0190	0·0597	0·175	0·490	2·64	4·68	6·87	8·25	8·35

Refs. p. 510

TABLE XXXIV. - SPECIFIC CONDUCTIVITY OF MOLTEN IODINE TRICHLORIDE[70]

t°C.	102·0	103·7	105·3	107·0	109·3	112·5	115·0
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	8·60	9·13	9·31	9·40	9·55	9·53	9·34
t°C.	122·9	127·0	131·0	135·5	139·0	142·7	146·5
$\kappa.10^3$ ohm^{-1} cm.$^{-1}$	8·15	6·73	4·52	2·39	1·29	0·69	0·36

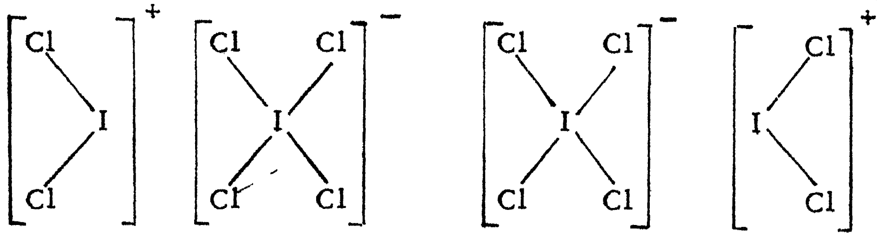


Fig. 3.

MESOMERIC FORMS OF IODINE TRICHLORIDE

The thermodynamic constants of iodine trichloride have been obtained from the pressure and composition of the vapour over the invariant system $ICl_3(s)$,-$ICl(l)$,$ICl(g)$,$Cl_2(g)$ at 25° and 35°C.[152] The equilibrium constant for reaction (47) is given by $K = p_{ICl}.p_{Cl_2}$ atm.[2] and the values at 25° and 35° are 1·09 × 10^{-3} and 4·36 × 10^{-3} atm.[2]; the corresponding heat content change and free energy change are $\Delta H^\circ_{298\cdot16}$ = 25·3 kg.-cal. mole^{-1} and $\Delta G^\circ_{298\cdot16}$ = 40·4 kg.-cal. mole^{-1}. These values lead[152] to the standard heat and free energy of formation according to equation (48): $-\Delta H^\circ_f$ = 21·15 kg.-cal. mole^{-1}; $-\Delta G^\circ_{298\cdot16}$ = 5·41 kg.-cal. mole^{-1}.

$$ICl_3(s) = ICl(g) + Cl_2(g) \qquad (47)$$
$$\tfrac{1}{2}I_2(s) + Cl_2(g) = ICl_3(s) \qquad (48)$$

The standard virtual entropy of solid iodine trichloride is[152] $S^\circ_{298\cdot16}$ = 41·1 g.-cal. deg.$^{-1}$ mole^{-1}.

Non-aqueous solutions of iodine trichloride, like those of the monochloride, have zero decomposition potential.[88,153,155] Solvents investigated include liquid sulphur dioxide, dichloroacetic acid;[153] bromine, arsenic trichloride, nitrobenzene;[88,153] and acetic acid.[88,153,155] The absence of a decomposition potential may be ascribed to the fact that the products of electrolysis are already in the solution as a result of thermal dissociation.[2] This is supported by spectrophotometric measurements on the (non-conducting) solutions of iodine trichloride in carbon tetrachloride, which indicate complete dissociation according to equation (49).[21]

$$ICl_3 \text{ (in } CCl_4) = ICl \text{ (in } CCl_4) + Cl_2 \text{ (in } CCl_4) \qquad (49)$$

The potential of an $I|ICl_3$ electrode has been measured by means of cells of the type:-[87]

(+I | aq. ICl_3 | N-KCl | Hg_2Cl_2 + N-KCl | Hg-) and
(+Pt | aq. ICl_3 | N-KCl | Hg_2Cl_2 + N-KCl | Hg-).

The standard electrode potential is E_{I/ICl_3} = 1·032 V. An iodine trichloride electrode has been set up in ether, hydrolysis at the ether/water interface being suppressed by the use of concentrated salt solutions.[154] The cell:-

$$(\mathrm{Pt}\ |\ \mathrm{ICl_3\ in\ Et_2O}\ |\ \mathrm{aq.\ ZnSO_4,LiCl}\ |\ \mathrm{Zn\text{-}Hg})$$

has an initial e.m.f. of 2·0 V. and this decreases to 1·8 V. over a period of one month.[154] The corresponding cell using magnesium instead of the Zn-Hg couple has an e.m.f. of 2·3 - 2·5 V. but the magnesium corrodes rapidly. The cells have the advantage of high e.m.f., large capacity and high rate of discharge, but they have a relatively short life. The solubility of iodine trichloride in anhydrous acetic acid is 33 weight-%; if traces of water are present, hydrolysis to iodic acid occurs rapidly.[155] The electrical conductivity of iodine trichloride in the anhydrous acid at 18°C. is given in Table XXXV; it is about five times as great as the conductivity of iodine monochloride in the same solvent (see page 489).[155] The electrical conductivity of solutions of iodine trichloride in methyl ethyl ketone varies with time, presumably owing to chemical reaction.[155] For example at 25°C. a solution of concentration $1{\cdot}95 \times 10^{-3}$ mole $\mathrm{l.}^{-1}$ had an initial conductivity of $3{\cdot}904 \times 10^{-5}$; this decreased to a minimum value of $1{\cdot}797 \times 10^{-5}$ in five minutes and then rose to a maximum value of $6{\cdot}271 \times 10^{-5}$ $\mathrm{ohm^{-1}\ cm.^{-1}}$ after 18 hours, after which it slowly diminished again. The nature of the ions present in non-aqueous solutions of iodine trichloride does not appear to have been satisfactorily elucidated.[153,155,157,158]

TABLE XXXV.- SPECIFIC CONDUCTIVITY OF IODINE TRICHLORIDE IN ACETIC ACID AT 18°C.[155]

wt.-% $\mathrm{ICl_3}$	0·0558	0·525	1·408	3·857	7·267
$\kappa.10^6\ \mathrm{ohm^{-1}\ cm.^{-1}}$	0·734	2·527	4·229	14·79	49·66
wt.-% $\mathrm{ICl_3}$	9·695	16·41	22·34	29·84	33·26
$\kappa.10^6\ \mathrm{ohm^{-1}\ cm.^{-1}}$	74·07	138·7	340·4	729·3	956·8

CHEMICAL PROPERTIES OF IODINE TRICHLORIDE

In the ternary system I - Br - Cl at 29·8°C., the solid phases are iodine trichloride, iodine monobromide and solid solutions of iodine monobromide in iodine; no ternary compound was found.[159] The degree of hydrolysis of iodine trichloride in water depends on the dilution and increases from 76% at 15 l. to 83·5% at 100 l. per mole $\mathrm{ICl_3}$.[160] The reactions occurring during hydrolysis are complicated, but have been formally represented by equation (50):-[155]

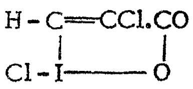
$$3\mathrm{ICl_3} + 6\mathrm{H_2O} = 9\mathrm{HCl} + \mathrm{HI} + 2\mathrm{HIO_3} \qquad (50).$$

Iodine trichloride, when dissolved in concentrated hydrochloric acid or in aqua regia, is a successful solvent for sulphidic minerals, especially pyrites.[162] With phosphorus trichloride the interhalogen forms the addition compound phosphorus iodine hexachloride[106] (see page 497).

The addition compounds of iodine trichloride with pyridine, quinoline and trimethylamine and their hydrates have been described.[163,164] The compounds with pyridine and quinoline are yellow and are readily soluble in water, ethanol or acetone.[164] Addition reactions with alkaloids have also been studied; nicotine takes up two moles of iodine trichloride for each nitrogen atom; sparteine takes up one mole in hot solution but two moles in the cold; pilocarpine takes up but one mole of iodine trichloride.[164] Iodine trichloride adds to acetylene to give the yellow crystalline 1,1,2-trichloro-1-iodoethylene, $\mathrm{ClCH{:}CHICl_2}$.[165] The addition reaction between iodine trichloride (in $\mathrm{CCl_4}$) and hydrocarbons is limited to those hydrocarbons with one or two isolated double bonds or two conjugated double bonds. With substances containing three or more conjugated double bonds and with sterols, hexachlorination occurs with the liberation of iodine.[166]

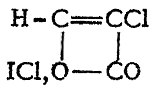
$$R + 2ICl_3 = RCl_6 + I_2 \qquad (51)$$

This reaction has been developed[166] into a procedure for estimating vitamin *D* to within ±5%. A solution of iodine trichloride in aqueous sodium chloride has been added to unsaturated fatty acids and esters; e.g. acetylenedicarboxylic acid $(\vdots C.CO_2H)_2$ is said to yield the iodosochloride of α-chloroacrylic acid, (VIII), by cyclization and decarboxylation,[167] but the product may also be formulated as the addition compound of iodine monochloride and a lactone, (IX).



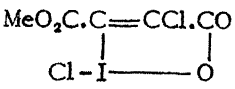
$$\begin{array}{l} H-C{=}CCl.CO \\ \;\;| \qquad\qquad\; | \\ Cl-I\text{———}O \end{array}$$

(VIII)



$$\begin{array}{l} H-C{=}CCl \\ \quad\;\; | \quad\; | \\ ICl,O-CO \end{array}$$

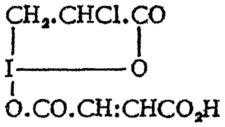
(IX)



$$\begin{array}{l} MeO_2C.C{=}CCl.CO \\ \qquad\qquad | \qquad\quad | \\ \qquad\; Cl-I\text{———}O \end{array}$$

(X)

The dimethyl ester of acetylenedicarboxylic acid $(\vdots C.CO_2Me)_2$, yields a product which is not decarboxylated, (X).[167] Fumaric acid $(:CHCO_2H)_2$ undergoes decarboxylation, elimination of hydrogen chloride, and cyclization to give the infusible solid (XI).[167]



$$\begin{array}{l} CH_2.CHCl.CO \\ | \qquad\qquad\;\; | \\ I\text{————}O \\ | \\ O.CO.CH{:}CHCO_2H \end{array}$$

(XI)

A Friedel–Crafts reaction between iodine trichloride and benzene in ether below 0°C. gives mainly chlorosubstitution products plus small amounts of iodobenzene.[168] Iodine trichloride alone, when added to benzene or its solution in carbon tetrachloride, reacts vigorously in such a way that chlorine substitutes simultaneously in adjacent positions in the nucleus (vicinal dichlorination).[169] Thus, the product of direct action yields 7% of chlorobenzene, 27% of *o*-dichlorobenzene (but no *p*-dichlorobenzene), 6% of 1,2,4,5-tetrachlorobenzene, and 3% of hexachlorobenzene. Similarly iodine trichloride (4 moles) and benzene (1 mole) in carbon tetrachloride yields 67% of *o*-dichlorobenzene and 32% of 1,2,4,5-tetrachlorobenzene. Anisole under the same conditions gives 40% of 3,4-dichloroanisole, and butyryl chloride gives 16% of the α,β-dichloro-derivative, MeCHCl.CHCl.COCl.[169] Geometrical considerations suggest that this vicinal dichlorination results from the transient formation in solution of the dimeric molecule I_2Cl_6 which is found in the solid state. Thiophen is completely chlorinated to octachlorotetrahydrothiophen.[52] Acetanilide yields *N*-dichloroiodoacetanilide, $PhN(ICl_2)CO.Me$.[170] Diaryliodonium compounds (e.g. Ph_2ICl) may be synthesized by the energetic reaction of phenyltin trichloride, $PhSnCl_3$, with iodine trichloride in dilute hydrochloric acid.[161]

$$ICl_3 + 2PhSnCl_3 = Ph_2ICl + 2SnCl_4 \qquad (52)$$

The same compound also results from the reaction of iodine trichloride with diphenyl mercury.[161]

$$ICl_3 + Ph_2Hg = Ph_2ICl + HgCl_2 \qquad (53)$$

These new methods of preparing iodonium salts are simpler and more rapid than methods previously described.

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SECTION XVII

THE OXIDES AND OXYACIDS OF CHLORINE

By C. C. ADDISON

CHLORINE MONOXIDE

The compound Cl_2O should properly be termed dichlorine monoxide, especially in view of the importance of the unit ClO in decomposition processes. In this account, however, the name chlorine monoxide is retained because of its widespread usage in chemical literature.

Preparation.

Chlorine monoxide is a true anhydride of hypochlorous acid, which it gives readily on solution in water: $Cl_2O + H_2O \rightleftharpoons 2HOCl$. It can be prepared by removing water from hypochlorous acid, using, for example, phosphoric oxide or anhydrous calcium nitrate. When an aqueous solution of the acid is shaken with carbon tetrachloride, the latter becomes brown-yellow in colour and contains dissolved chlorine monoxide. These distribution experiments indicate that chlorine monoxide is about 8 times as soluble in carbon tetrachloride as in water, and that in a 0·2N. solution of hypochlorous acid there is about 0·02% of chlorine monoxide.[1] When a current of air is passed through a solution of hypochlorous acid, chlorine monoxide is carried away in the air stream.[2,3] Pure anhydrous chlorine monoxide may be prepared by distilling a 25% solution of hypochlorous acid in vacuo, over mercuric oxide. The distillate is collected in three receivers in series, cooled to 0°, -20° and -80°. The first two receivers effectively remove hypochlorous acid, and chlorine monoxide condenses in the third receiver.[1] The standard laboratory method of preparation, by reaction of chlorine with mercuric oxide, has already been described (Mellor,II,240). This method has been adapted for large-scale production by passing over mercuric oxide a mixture of chlorine with an inert diluent such as carbon tetrachloride. The monoxide is removed, and the basic mercuric chloride produced is treated with alkali to reprecipitate mercuric oxide, which may be used again.[4] An important general method of preparation employs the reversible hydrolysis of chlorine: $Cl_2 + H_2O \rightleftharpoons HOCl + HCl$. In order to maintain the forward reaction, the hydrochloric acid must be removed and this may be done in a variety of ways. If chlorine is passed into a solution of potassium hypochlorite, the OCl^- ions are converted to HOCl: $OCl^- + HCl \rightarrow HOCl + Cl^-$. When the solubility of hypochlorous acid is exceeded, decomposition occurs and continued passage of chlorine into the solution gives chlorine monoxide. The hydrogen chloride can also be removed by sodium sulphate or phosphate, when the SO_4^{2-} and HPO_4^{2-} ions give HSO_4^- and $H_2PO_4^-$; or by sodium carbonate or bicarbonate, when the ions CO_3^{2-} and HCO_3^- yield CO_2 and H_2CO_3. This method has been developed on an industrial scale; an alkali metal carbonate or bicarbonate is treated with chlorine at 200°, or the silicate, hydroxide or phosphate is treated at temperatures not less than 150°, when gaseous chlorine monoxide is evolved.[5]

Physical Properties.

A determination of the freezing point from cooling curves[7] gave the melting point as -116° ± 1°. When, however, the gas was carefully purified by drying over phosphoric oxide followed by liquefaction and the removal of chlorine or air present by distilling off part of the chlorine monoxide, a sample was obtained melting at −120·6°C.[6] From vapour pressure studies, the boiling point is found to be 2·0° at 760 mm. The Trouton constant is 22·5, so that little or no association can take place in the liquid state. Measured by a calorimetric method, the heat of solution of 1 mol. of chlorine monoxide in 2072 molecules of water is 8·737 kg.-cal./mol.[8] A plot of the logarithm of the equilibrium constant K against $1/T$ for the reaction $Cl_2O_{(g)} + H_2O \rightarrow 2HOCl$ aq. indicates, however, that the heat of solution is sensitive to temperature to a surprising degree; at 5°, 10° and 18°, ΔH for this reaction is 9·3, 11·4 and 16·0 kg.-cal. respectively.[12] This variation is no doubt responsible for the apparent discrepancies in several of the calculated thermodynamic functions which include this quantity. The plot of the logarithm of the vapour pressure of chlorine monoxide (p mm.) against $1/T$ gives a straight line represented by $\log_{10}p = -1373/T + 7{\cdot}87$. From the slope of this line, the latent heat of evaporation is 6·2 kg.-cal./mol.[7] In common with other oxides of chlorine, chlorine monoxide is endothermic and is not obtained directly from the elements. Heats of formation are therefore calculated values, and show some discrepancy; those quoted are 16·24,[8,9] 18·64[11] and 23·5[12] kg.-cal./mol. From measurement of the heat liberated when chlorine monoxide explodes, a value of 25·1 kg.-cal./mol. was calculated.[10] The entropy of chlorine monoxide gas at 25° and 1 atmosphere is 67·9 g.-cal./degree.[13] The true value may be somewhat higher owing to possible errors in the values employed for the heat of formation of chlorine monoxide.[12]

Partial pressures of chlorine monoxide over its aqueous solutions have been measured for a range of concentrations and temperatures, and are shown in Table I.[12]

TABLE I. - PARTIAL PRESSURE OF CHLORINE MONOXIDE OVER ITS AQUEOUS SOLUTIONS

HOCl concn. (molal)	p.mm. at 3·46°C.	HOCl concn. (molal)	p.mm. at 9·92°C.	HOCl concn. (molal)	p.mm. at 19·98°C.
1·76	1·27	1·22	0·918	0·861	1·11
2·49	2·54	1·44	1·37	1·35	2·72
3·60	5·31	1·89	2·24	1·92	5·61
4·88	10·10	2·88	5·29	2·64	10·78
5·97	15·36	3·26	6·71	3·03	14·41
6·90	19·33	4·16	10·88	3·77	22·82
9·48	39·00	5·25	17·53	4·92	40·61
11·11	57·02	6·64	29·10	5·40	49·48
13·14	88·40	7·89	44·20	6·23	67·88
14·95	126·1	8·81	57·83	6·80	80·82
19·95	247·6	9·84	75·62	7·01	87·49

Chlorine monoxide and water form a pair of partially miscible liquids. The solid phase formed from solutions of monoxide concentration greater than 11·7 mol.% has the composition $HOCl,2H_2O$.[6] The solubility of chlorine monoxide in water is given in Table II, which illustrates the rapid decrease in solubility with increasing temperature.[12]

A nomograph has been described for the correlation of solubility, partial pressure and temperature in the chlorine monoxide-water system.[14] Values for the equilibrium constant K (expressed as $p_{Cl_2O} \times a_{H_2O}/(a_{HOCl})^2$) for the equilibrium $Cl_2O\ (g) + H_2O\ (l) \rightleftharpoons 2HOCl\ (aq)$ are given below Table II.[12]

The partial pressure values given above have been combined with data for this equilibrium to evaluate the Henry's Law constant: at 3·46°,

TABLE II. - SOLUBILITY OF CHLORINE MONOXIDE IN WATER (g.Cl_2O/100 g.H_2O)

Partial pressure p Cl_2O,mm.	Solubility		
	0°	10°	20°
1	7·6	5·2	3·5
5	16·7	12·3	8·0
10	23·7	17·4	11·1
30	40·7	29·2	18·7
50	52·4	36·2	23·7
70	60·2	41·4	27·7

Temp. °C.	3·46	6·00	9·92	16·00	19·98
K	0·41	0·48	0·62	1·01	1·47

expressing pressure in mm. of mercury, the constant is 0·00937 ± 0·00005.

Photochemical Decomposition.

Exposure to light brings about photochemical decomposition of chlorine monoxide. On exposure to light of mean wave-length 4600 A., two molecules of chlorine monoxide are photochemically decomposed for each quantum of light absorbed, *i.e.* $2Cl_2O + h\nu \rightarrow 2Cl_2 + O_2$.[15] This has been confirmed for light of wave-length 4360 A. and 4050 A.[16] The effective light is that also absorbed by chlorine; if a mixture of chlorine and chlorine monoxide is irradiated, the decomposition of the monoxide is proportional to the total amount of energy absorbed by the mixture, so that the monoxide decomposition is sensitized by energy absorbed by chlorine.[16] Traces of chlorine are almost always present as an impurity, but since the rate of decomposition of purified monoxide is proportional to the amount of light absorbed, it is independent of whether chlorine or chlorine monoxide is the initial absorbent. It is independent of the chlorine pressure, and, over wide limits, of the chlorine monoxide pressure also.[17] The 10° temperature coefficient of the reaction is 1·09 at 10°,[16] 1·1 at room temperature,[17] and continues to rise with increasing temperature. A small amount of chlorine dioxide is formed during photodecomposition. Its presence is shown by the appearance of characteristic band spectra when the reaction starts.[16] An unidentified higher oxide of chlorine is also formed.[17] The absorption spectrum of chlorine monoxide has been measured over the range 2200 - 8500 A.[17,21] Absorption begins at 6600 A., and is continuous to 2200 A. under pressures of 10 - 600 mm. (See Fig. 3, page 650).

In the reaction mechanisms proposed for the photochemical decomposition, the molecule ClO features prominently as an intermediate compound. The absorption beginning at 6600 A. corresponds to $Cl_2O \rightarrow ClO + Cl$, and the maxima at 5300 and 4100 A. represent the same dissociation at other stages of excitation. The maximum occurring at 2560 A. arises from the dissociation $Cl_2O \rightarrow Cl + Cl + O$.

The photochemical decomposition of chlorine monoxide in solution in carbon tetrachloride differs from that in the gaseous phase.[19] At wave-length 4358 A. decomposition is accompanied by the formation of considerable amounts of chlorine dioxide. For example, in 0·014 to 0·054 molar solutions of the monoxide, chlorine dioxide is produced at the initial rate of 0·35 mol. per quantum absorbed. The decomposition is generally slower than in the gaseous state, but 1·8 mols. of chlorine monoxide can be decomposed per quantum absorbed.[19] It has been suggested that the quantum yield is smaller because the reactions $Cl + Cl \rightarrow Cl_2$, and $Cl + ClO \rightarrow Cl_2O$ occur more frequently in solution than in the gaseous state, and compete with the reaction $Cl + Cl_2O \rightarrow Cl_2 + ClO$.[17] A quantum yield of unity in this system[20] has been attributed to impurities in the carbon tetrachloride, which take up the Cl atoms before thay can react with Cl_2O molecules.[18]

The ClO radical is also an important intermediate in the decomposition of chlorine dioxide (see page 529) and explains the chlorine-sensitized photochemical decomposition of ozone.[18] Its heat of formation has been calculated as $Cl + O \rightarrow ClO$ + 30·4 kg.-cal.[22] The electron affinity of the ClO radical, *i.e.* the work required to remove an electron from the hypochlorite ion, is approximately 68 kg.-cal.[23]

Chlorine monoxide undergoes bromine-sensitized decomposition in green light.[24] On exposure to light of wave-length 5460 A. decomposition involving short chains occurs, and is accompanied by an appreciable dark reaction. The quantum yield at 19° is 4·3, and the results are satisfactorily explained by the mechanism discussed above,[17] for the unsensitized reaction. The photodecomposition of chlorine monoxide is accelerated by the addition of hydrogen up to the stage where the secondary reaction $H_2 + Cl_2 \rightarrow 2HCl$ becomes prominent. Chlorine and oxygen are again the initial reaction products, though small amounts of hydrogen chloride and water are formed; ultimately all the chlorine is converted to hydrogen chloride. The ClO radical is more important than the H atom in continuing the reaction chain.[25]

Thermal Decomposition.

This is an interesting problem in kinetics which has been the subject of much discussion and research. Chlorine monoxide is highly explosive if heated rapidly or overheated locally, but under conditions of careful temperature control the thermal decomposition proceeds at a conveniently measurable rate between about 60° and 140°.[26-31] This rate is measured by registering the pressure change; at the lower temperatures total decomposition requires

TABLE III. - THERMAL DECOMPOSITION OF CHLORINE MONOXIDE

Temp. 100°C. Initial Cl_2O pressure 412·8 mm.		Temp. 110°C. Initial Cl_2O pressure 490 mm.	
t mins.	Δp mm.	*t* mins.	Δp mm.
0	-	0	-
40	11·5	40	52·7
80	42·3	60	123·8
120	96·3	80	182·5
150	137·7	90	201·0
170	159·0	100	211·8
180	168·0	120	225·8
190	174·6	140	233·6
200	180·1	160	240·4

Temp. 130°C. Initial Cl_2O pressure 436 mm.		Temp. 140°C. Initial Cl_2O pressure 372 mm.	
t mins.	Δp mm.	*t* mins.	Δp mm.
0	-	0	-
10	52·3	4	24·5
16	125·0	8	89·1
19	154·5	10	121·3
22	175·4	12	144·8
25	190·0	14	160·6
28	199·1	16	171·4
31	206·7	18	186·0
32·5	216·9		

12–24 hours, but at higher temperatures is complete within a few minutes. Table III shows the increase in pressure Δp after time t at various initial temperatures and pressures; $2\Delta p$ represents the quantity of chlorine monoxide decomposed.[31]

The thermal reaction is homogeneous, and the rate is not influenced if the area of glass surface is greatly increased by adding glass wool to the reaction vessel. The rate accelerates as the reaction proceeds, and it was at first thought that this might be due to autocatalysis by the chlorine and oxygen produced. The acceleration persists, however, in the presence of excess of oxygen or chlorine and the reaction rate is not appreciably influenced by a five-fold excess of dry air, oxygen or nitrogen.[27] The rate of decomposition of chlorine monoxide varies with time in the same manner as does the oxidation of ethane by oxygen;[29] this may be related to the postulate that nascent oxygen is an autocatalyst in the thermal decomposition of chlorine monoxide,[28] but this suggestion is not in keeping with modern developments. Excess oxygen has some effect on the explosive properties, however. At 1 atm. pressure and 23°, mixtures of the monoxide and oxygen do not explode if they contain less than 23·5% by volume of monoxide. Between 25 and 30% monoxide the explosions are weak; a hot spark is required to start the explosion, and a yellow band of light moves relatively slowly along the reaction tube. Above 30% monoxide, the mixture explodes with violence emitting an orange flash which extends the length of the reaction tube.[30]

The mechanism of the reaction has not been determined with certainty. The reaction rate (excluding the slow initial induction period) is proportional to the initial pressure of the chlorine monoxide, *i.e.* $-d(Cl_2O)/dt = k[Cl_2O]$,[31] at temperatures between 100° and 130°[31] and at 131·3°.[27] At 140°[31] $-d(Cl_2O)/dt = k[Cl_2O]^{0\cdot 75}$. The temperature coefficient is 2·03 for a 10° rise,[27] and it would appear that bimolecular reactions are important in the decomposition. The shape of the pressure-time curves has been interpreted both on the basis of consecutive bimolecular reactions,[32-36] and as a chain reaction.[31,37,38] In the first case, the acceleration is attributed to the operation of at least two consecutive reactions, each essentially bimolecular, of which the first produces a pressure change less than that given by the subsequent reactions. The separate stages of the reaction are not clearly defined, so that the velocity constant k and the activation energy E for the separate reactions must be similar. If log k is plotted against $1/T$, then $E = 21000$ g.-cal.[32] These consecutive reactions would no doubt involve the formation of other oxides of chlorine. In contrast to this approach, the observation that an explosion frequently occurred towards the end of the slow thermal decomposition led to the postulate that the decomposition was a complicated chain reaction, in which the Cl atom and the ClO radical were the chain carriers.[31,37,38] A possible mechanism for chain propagation in the temperature range 100°–130° is as follows:-[31]

$$\begin{gathered}
Cl_2O + Cl_2O \rightarrow ClO_2 + Cl + Cl_2 \\
Cl + Cl_2O \rightarrow ClO + Cl_2 \\
ClO + Cl_2O \rightarrow ClO_2 + Cl_2 \\
ClO_2 \rightarrow ClO + O \\
ClO_2 \rightarrow Cl + O_2 \\
Cl_2O + O \rightarrow 2ClO \\
ClO + ClO \rightarrow Cl_2 + O_2
\end{gathered}$$

At 140°, when the reaction rate changes, the first two steps may be replaced by $Cl_2O + Cl_2O \rightarrow 2ClO + Cl_2$. It is, however, difficult to reconcile this picture with the fact that added air, carbon monoxide or carbon dioxide, which might be expected to interfere with these processes, do not appreciably modify the thermal decomposition.[38] The heat of dissociation of chlorine monoxide, measured directly by sparking the gas in a calorimeter, is 21735 ± 560 g.-cal.[39] (A value of 25100 ± 100 g.-cal. is also reported).[40] These values tend to support the chain mechanism, since the energy released on bimolecular collision would give to the product molecules an energy in excess of the activation energy, resulting in immediate explosion.[39] During these experiments it was also observed that when chlorine monoxide was pure, or contaminated only with relatively small quantities of chlorine, no explosion was obtained on sparking unless the pressure was atmospheric or greater. On passing a spark in the gas at low pressures, a blue glow appeared at the electrodes and spread for only a short distance, so that if reaction chains exist they do not propagate far at low pressures.[39] If a tube containing liquid chlorine monoxide is dropped from a great height on to a cement floor it does not detonate, whereas chlorine dioxide detonates violently even at -100°.[39] The thermal decomposition of chlorine monoxide in solution in carbon tetrachloride has the same rate and temperature coefficient as in the gaseous state, so that it appears likely that in both cases decomposition occurs by the same mechanism.[41]

Analysis.

Samples for analysis may be condensed into small tubes cooled in liquid air, and the tubes sealed. A tube is then broken into a concentrated solution of potassium iodide containing a known quantity of hydrochloric acid. Iodine is liberated:-

$$Cl_2O + 4KI + 2HCl \rightarrow 4KCl + H_2O + 2I_2$$

and may be titrated with sodium thiosulphate. If the acid is also titrated with standard sodium hydroxide, the ratio of the two titrations gives a measure of the purity of the chlorine monoxide.[39]

Dipole Moment and Structure.

This has been determined from the dielectric constant ϵ of dilute solutions of chlorine monoxide in carbon tetrachloride (Table IV).[42]

TABLE IV. - DIELECTRIC CONSTANT ϵ, AND MOLAR POLARIZATION P OF CHLORINE MONOXIDE IN DILUTE SOLUTION IN CARBON TETRACHLORIDE

Temp. °C.	Mol. Fraction					P c.c.
	0·00597	0·01197	0·01952	0·02838	0·0390	
-18	$\epsilon =$ 2·3160	2·3196	2·3239	2·3294	2·3367	25·42
-8	2·2952	2·2988	2·3025	2·3078	2·3146	24·56
3	2·2728	2·2761	2·2796	2·2843	2·2904	24·16
14	2·2505	2·2535	2·2568	2·2609	2·2662	23·72
24	2·2305	2·2330	2·2360	2·2399	2·2441	23·14

These values lead to a dipole moment of 0·78 ± 0·08 × 10^{-18} e.s.u. for chlorine monoxide, and the molecule is therefore not linear. The structure has been studied by electron diffraction, and the close agreement between two separate investigations is shown in Table V.

TABLE V. - STRUCTURE OF CHLORINE MONOXIDE

	ref. 43	ref. 44
Cl-O bond length (A.)	1·71 ± 0·02	1·701 ± 0·02
Angle Cl-O-Cl	111° ± 2°	110·8 ± 1·0
Cl-Cl distance (A.)	2·82 ± 0·03	2·791 ± 0·02

The Cl–O bond length is only slightly greater than the sum of the two covalent radii (1·65 A.); the Cl–O–Cl angle is a little larger than the angle for water (105°).

Chemical Properties.

Little work in addition to that already discussed (Mellor,II,241) has been published. The overall reaction with ammonia is given by:-

$$3Cl_2O + 10NH_3 \rightarrow 6NH_4Cl + 3H_2O + 2N_2$$

which has been found to proceed firstly by the reaction:-

$$3Cl_2O + 2NH_3 \rightarrow N_2 + 3H_2O + 3Cl_2$$

followed by:-

$$3Cl_2 + 8NH_3 \rightarrow 6NH_4Cl + N_2.$$ [45]

Chlorine monoxide often explodes violently in contact with organic compounds, though its behaviour in this respect is unpredictable. Controlled reaction can be achieved by passing the monoxide at a low temperature into dilute solutions of the organic compound in carbon tetrachloride.[46] The products of reaction with organic compounds are frequently the same as those given by chlorine; for example, acetone gives the monochloro derivative $ClCH_2.COCH_3$, acetoacetic ester gives the compound $CH_3CO.CHCl.COOC_2H_5$, and *cyclo*hexane gives a mixture of chloro-derivatives. With unsaturated organic compounds the reactions are more complicated; trichloroethylene reacts to give the compounds $Cl_3C.CHCl_2$ and $Cl_3C.CHO$ and an octachlorodiethyl ether $(Cl_3C.CHCl)_2O$. Other reactions in which the products are not so well characterized have been described.[46]

The oxidation of sulphite ion to sulphate by chlorine monoxide has been measured in the presence of ^{18}O as tracer element, whereby it is possible to determine to what extent the solvent (water) or the oxidizing agent itself provides the oxygen atoms gained by the reducing agent. In a typical experiment, 0·25 ml. of a 0·4M. solution of chlorine monoxide in carbon tetrachloride was added to 0·1M-hydrochloric acid containing 1 ml. of a 0·1M. solution of sulphur dioxide (labelled with ^{18}O). The number of oxygen atoms in the sulphate produced which were derived from the oxidizing agent (chlorine monoxide) per molecule of oxidizing agent reacting (*n*) was only 0·36. Since hypochlorous acid may also play some role in the mechanism of oxidation, 0·2 ml. of 1M-HOCl was added to 5 ml. of 0·02M-sulphur dioxide in 0·2M-hydrochloric acid. The value of *n* was only 0·05, which suggests that there is no oxygen atom transfer from hypochlorous acid to the sulphite ion.[47]

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CHLORINE DIOXIDE

Preparation.

The increasing industrial application of chlorine dioxide as a bleaching agent, particularly for paper and flour, and its use as an antibacterial agent during the past two decades, has stimulated work on its safe and efficient preparation. Most of this recent work is concerned with modifications of older and well-known methods designed to eliminate the hazard of explosion and to effect a good separation of chlorine dioxide from other reaction products, particularly chlorine.

The reaction between concentrated sulphuric acid and a solid chlorate by which chlorine dioxide was first discovered (Mellor,II,287), involves great dangers from explosion. References to the reaction are still found, although adequate precautions are always necessary, and emphasis is laid on the efficiency of the process and the utilization of by-products.[9] By diluting the reactants in various ways the reaction can be more readily controlled; the removal of the chlorine dioxide in a stream of inert gas is especially valuable. A mixture of 300 ml. of 25% sulphuric acid, 10 g. of charcoal and 100 g. of sodium chlorate gives a yield of 80% of chlorine dioxide when air is passed through the reaction vessel for one hour at 500 ml./minute and the temperature is maintained at 90°.[1] Alternatively, air may be blown through a solution of sodium chlorate in concentrated sulphuric acid at 60°, when chlorine dioxide low in chlorine content (<3%) is evolved.[2] The addition of sodium chlorate in small amounts to concentrated sulphuric acid, through which a stream of an unreactive gas (e.g. air or nitrogen) is passing, is a successful procedure.[3]

The reactants may also be diluted by moistening the chlorate with water and then mixing with some material, such as pumice or gypsum, indifferent to chlorate or sulphuric acid; 96% sulphuric acid is then added.[4,5] The main reaction is:-

$$3HClO_3 \rightarrow 2ClO_2 + HClO_4 + H_2O.$$

By carrying out the reaction between potassium chlorate and sulphuric acid in the presence of undecylenic acid, the proportion of chlorine dioxide produced is much less; it was claimed that the disproportionation reaction, $2Cl_2O_5 \rightarrow Cl_2O_7 + Cl_2O_3$, was favoured at the expense of the reaction, $3Cl_2O_5 \rightarrow Cl_2O_7 + 4ClO_2$, and that the spectra of the products showed the presence of 'chlorous anhydride' Cl_2O_3.[6] Attempts to repeat these observations were quite unsuccessful. The reaction always resulted in explosion even when carried out at temperatures as low as -78°; only when the reactants were mixed with four times their bulk of sand at the temperature of liquid air did no explosion occur. Spectroscopic examination of the resultant gases gave the spectrum of chlorine dioxide only, with no trace of any other oxide of chlorine.[7,8] Other acids may be used together with, or in place of, sulphuric acid.[10] An $HCl-H_2O-H_2SO_4$ mixture, in the ratio 85:6.9 reacts with a concentrated (33%) solution of sodium chlorate evolving chlorine dioxide and chlorine. The optimum temperature is 49°-71°, and an inert gas (air, nitrogen, carbon dioxide) removes the chlorine dioxide from the reaction mixture.[11] Other modifications include the reaction of sodium chlorate and chloride with sulphuric-hydrochloric acid mixtures,[12] and the action of hydrochloric acid alone on magnesium chlorate[13] and on sodium chlorate.[14,15] The latter reaction can be represented thus:-

$$2NaClO_3 + 4HCl \rightarrow 2ClO_2 + Cl_2 + 2H_2O + 2NaCl;$$

the by-product sodium chloride can then be electrolyzed to yield more sodium chlorate for a cyclic process. A similar process employs an electrolytic chlorate liquor (500 g. $NaClO_3$ + 75 g. NaCl/litre) which is treated with hydrogen chloride, and maintained at 55-65° until 28% of the chlorate is consumed. The gaseous product contains 59% chlorine dioxide, the remainder being chlorine; the spent liquors are re-electrolyzed to restore the chlorate concentration.[16]

A method very suitable for industrial production of chlorine dioxide involves the reaction of chlorine with an alkali or alkaline earth metal chlorite, the overall reaction being $2NaClO_2 + Cl_2 \rightarrow 2NaCl + 2ClO_2$.[17,18] The method can be adapted for either continuous or batch operation, and can be a wet or dry process. Commonly, the solid chlorite is packed into steel towers, lined with some inactive material such as stone or glass, and chlorine gas diluted with nitrogen is passed through the tower. Chlorine-free chlorine dioxide is readily obtained by this method, since any residual chlorine can be removed by recycling the gas or by passing it through fresh chlorite.[17-24] Alternatively, chlorine dioxide is produced by passing diluted chlorine through an aqueous solution of a chlorite.[22,25-30] Adequate control of the reaction is possible by incorporating an explosion chamber,[19] by controlling the pressure of the circulating gases,[24,28] and by other mechanical methods.[17] Chlorine dioxide may also be prepared by treating aqueous sodium chlorate with chlorine.[31]

The reduction of a metal chlorate by sulphur dioxide is another general method of preparation.[32-46] The aqueous solution of chlorate (e.g. sodium, calcium or magnesium chlorate) is allowed to pass down a tower up which a mixture of sulphur dioxide and air is passed. In a typical case, aqueous sodium chlorate solution (690 g./l.) was fed into a reaction tower at 990 ml./hour, and air containing 14·8% of sulphur dioxide was passed in at the rate of 675 g. SO_2/hour. Chlorine dioxide was produced at the rate of 282 g./hour, representing a yield of 68% based on the chlorate used. The product, much diluted with air, contained chlorine dioxide and chlorine in the ratio 14 : 1.[39] Some chlorine is usually produced in this process, although the amount varies with conditions. Sulphur dioxide suitably diluted may be obtained by using the total gases evolved from a sulphur burner. The reaction has been carried out using the chlorate in the form of a paste containing just sufficient water to permit reaction.[35] In this process the sulphur dioxide provides both the acid solution and the reducing agent, and the overall reaction:-

$$2HClO_3 + SO_2 \rightarrow 2ClO_2 + H_2SO_4$$

is believed to proceed in the two steps:-

$$HClO_3 + H_2SO_3 \rightarrow HClO_2 + H_2SO_4$$
$$HClO_2 + HClO_3 \rightarrow 2ClO_2 + H_2O.$$

At room temperature there is little reaction of sulphur dioxide with either chlorine dioxide or chlorous acid; high temperatures at which reaction does occur are therefore avoided.[33,39] It is often advantageous to carry out this reduction in the presence of added mineral acid. Sulphuric acid is usually employed, although hydrochloric acid may be used.[46] For example, the reaction of diluted sulphur dioxide with a 2 M-sodium chlorate solution in 6-9 N-sulphuric acid at 10°-40° gives yields above 90%, and the chlorine content of the chlorine dioxide is less than 5%.[34,42] Excessive dilution reduces the yield of chlorine dioxide,[35] since the second stage represented above does not then proceed so far to the right.

The above reduction method may be refined to give chlorine dioxide substantially free from chlorine by the use of two reducing agents.[47-50] In addition to the major reaction:-

$$ClO_3^- + 2H^+ + e^- \rightarrow ClO_2 + H_2O,$$

chlorine is produced by the side reactions:-

$$ClO_2 + 4H^+ + 5e^- \rightarrow Cl^- + 2H_2O,$$
$$\text{and } Cl^- \rightarrow \tfrac{1}{2}Cl_2 + e^-$$

If reduction is carried out with a primary reducing agent having an oxidation-reduction potential above +1·0V., the side reactions can be almost eliminated. For the oxidation-reduction couple, a solution of chromium (Cr^{3+} and Cr^{6+}) or thallium (Tl^+ and Tl^{3+}) salts is suitable, but oxides or salts of arsenic, antimony and bismuth in the lower valency levels may also be used. Under suitable conditions reaction at 70° will convert part of the chlorate to chlorine monoxide without the formation of chlorine. A secondary reducing agent (sulphur dioxide or compounds of bivalent sulphur), having an oxidation-reduction potential less than +1·0V., is then used below 40° to restore the primary agent to its reducing form without appreciable reduction of the chlorate. Further chlorate may then be added and the process repeated.[47-50]

The reduction of chlorates by organic reagents has the advantage that the carbon dioxide also produced serves to dilute the chlorine dioxide and so to minimize the risk of explosion. Oxalic acid is commonly used, and a mixture with solid chlorate and a very small quantity of water readily evolves chlorine dioxide on heating.[5,51,52] To control the reaction the mixture is diluted with inert material such as diatomaceous earth,[53] calcium sulphate[54] or silica.[55] Sulphuric acid may also be added to the mixture, in which case the gas produced contains carbon monoxide also.[52,53,55] In the presence of sulphuric acid, aldehydes reduce chlorates to chlorine dioxide.[5,56] Chlorites are also reduced by aldehydes, but in this case the reduction should be carried out in the absence of acid at a pH below 9. Since the quantity of aldehyde required is small compared with the amount of chlorate or chlorite reduced, the reaction may involve auto-oxidation of the chlorite induced by aldehyde, or it may be a coupling reaction in which aldehyde reacts and is reformed.[57] Formaldehyde is usually employed, but other reducing agents that have been used include formic acid and carbohydrates,[5] and citric acid.[51] Acid anhydrides readily liberate chlorine dioxide from alkali or alkaline earth chlorites. At pH 4 and room temperature, the rate at which chlorine dioxide is liberated from a 0·1M. solution of sodium chlorite is increased thirty fold when the solution is made as little as 0·005 molar in acetic anhydride. Chlorine dioxide is liberated when air containing acetic anhydride is passed over flaked sodium chlorite. Again, the passage of moist air over a powdered mixture of sodium chlorite and phthalic anhydride generates chlorine dioxide. Many other anhydrides are similarly effective.[60] These facts have led to the formulation of solid mixtures, which can be stored and will evolve chlorine dioxide on adding water. Such mixtures usually contain 1 mol. of chlorite and 0·1 to 1 mol. of the anhydride, together with a desiccant (sodium hydroxide, calcium chloride) to stabilize the mixture, and a solid diluent (sodium carbonate, bicarbonate or phosphate). Chlorine dioxide is obtained by passing moist air over the solid, or by passing air or other inert gas through a solution of the solid in water.[30,58-60] In another modification of this method, chlorine dioxide is prepared from a chlorite, formaldehyde, a weak acid (formic, acetic or boric) and a sodium salt of the weak acid (e.g. sodium acetate).[61]

Both chlorates and chlorites react with nitrogen dioxide to give chlorine dioxide. A metal chlorate is dissolved in nitric acid (containing not less than 35% by weight HNO_3) and a gaseous mixture of nitrogen dioxide and an inert diluent gas passed into the solution. The following reaction occurs:-

$$ClO_3^- + NO_2 \rightarrow NO_3^- + ClO_2.$$

This may be an interesting example of oxygen ion transfer, and the mechanism of the reaction merits further study. If more dilute nitric acid is used (<35%) some hydrolysis of nitrogen dioxide occurs, giving nitrous acid and nitric oxide, which leads to contamination of the chlorine dioxide with chlorine. The optimum temperature for the solution reaction is 15 - 35°.[62,63] The reaction can also be carried out by passing diluted nitrogen dioxide over a solid metal chlorate in the presence of a little moisture.[64] The reaction with chlorites is similar:-[66]

$$ClO_2^- + NO_2 \rightarrow ClO_2 + NO_2^-.$$

Since the presence of nitrite in solution contaminates the chlorine dioxide with chlorine, this reaction is carried out with solid chlorite. An air stream containing 1 - 2% of nitrogen dioxide is passed through a column of solid sodium (or calcium) chlorite at 20 - 50°; the nitrogen dioxide releases an equimolar quantity of chlorine dioxide. Solid sodium nitrite remains in the column, and may be used to generate further supplies of nitrogen dioxide. Suitably dilute mixtures of nitrogen dioxide with air are also obtained by passing air through an electric arc.[65-67]

Liberation of chlorine dioxide from chlorates or chlorites may be effected by the use of oxidizing agents. The processes are less clearly defined because the oxidizing agent may bring about either direct oxidation or auto-reduction. For example, chlorine dioxide is produced by reaction of a metal chlorate with sodium or potassium persulphate in the presence of dilute sulphuric acid (pH <1 and temperature <50°)[69] or with hydrogen peroxide (temperature <70°).[70] Using a chlorite of an alkali or alkaline earth metal, addition of acid is unnecessary; the chlorite is dissolved in water (pH between 3 and 11) and the solution treated at 20° - 65° with persulphate.[68] On the other hand, if moderately hot acid solutions are used, the slow evolution of chlorine dioxide which would normally occur is effectively repressed by the addition of hydrogen peroxide or compounds which yield hydrogen peroxide on hydrolysis. The extent of repression varies appreciably with pH and the temperature of the solution.[71]

Reaction of silver chlorate with chlorine is a useful laboratory method which gives chlorine dioxide sufficiently pure for measurement of its physical properties.[72] The silver chlorate is packed into U-tubes through which dry chlorine is passed. Reaction is not appreciable below 80°, but proceeds smoothly at 90°:-[72]

$$2AgClO_3 + Cl_2 \rightarrow 2ClO_2 + O_2 + 2AgCl.$$

Residual chlorine may be removed by freezing the gaseous products; some chlorine condenses with the frozen chlorine dioxide but is readily removed when the condensate is subjected to low pressure. In the original treatise (Mellor,II,281) reference is made to the possibility that the oxide Cl_2O_3 (called 'chlorine trioxide') might be produced by this reaction, although its existence is doubted. Careful examination of the products of this reaction[72] (and others said to produce such an oxide) have proved beyond doubt that no oxide of empirical formula Cl_2O_3 has yet been isolated.

64–93% yields of chlorine dioxide (based on chlorite consumption) can be obtained by the reaction of nitrogen trichloride with sodium chlorite:-[73]

$$NCl_3 + 3H_2O + 6NaClO_2 \rightarrow 6ClO_2 + 3NaCl + 3NaOH + NH_3$$
$$\text{or } 2NCl_3 + 6NaClO_2 \rightarrow 6ClO_2 + 6NaCl + N_2.$$

Nitrogen trichloride–chlorine dioxide mixtures are used in flour bleaching. For such purposes the second (dry) reaction is preferred, and nitrogen trichloride gas is passed through a bed of granular sodium chlorite. A suitable gas mixture can also be prepared in a single stage by passing an air stream charged with hydrogen chloride through a bed of finely divided ammonium chloride and potassium chlorite in 1:6 mol. ratio, dispersed on some inert carrier.[74]

A novel method of preparation involves the direct decomposition of manganous chlorate. If its aqueous solution is heated to 50–90° it becomes unstable (presumably the chlorate is reduced at the expense of the manganese) and the chlorine dioxide can be continually removed in a stream of a chemically inert gas.[75] If chlorine dioxide is required in admixture with carbon dioxide (as in the sterilization of storage spaces refrigerated by carbon dioxide) it may be made by passing moist carbon dioxide through a bed of granular sodium chlorite. The concentration of chlorine dioxide in the gaseous product varies with the moisture content of the carbon dioxide used.[76] Electrolytic methods have also been used to prepare chlorine dioxide.[77,78] A product free from chlorine is obtained by electrolysis (using a carbon anode and copper cathode) of an aqueous solution of an alkali or alkaline earth metal chlorite in the presence of excess of the metal chloride.[77] Oxygen is the main anodic product obtained on electrolyzing perchloric acid solutions, but when an 11·4N. solution was electrolyzed at a current density of 0·75 amp./cm.^{2}, chlorine dioxide and chloric acid were also formed.[78] This is quantitatively accounted for by the reactions:-

$$ClO_4^- \rightarrow ClO_2 + O_2 + e^-$$
$$\text{and } 2ClO_2 + 2OH^- \rightarrow 2HClO_3 + 2e^-.$$

In most processes for the production of chlorine monoxide, chlorine is the main impurity, and methods for its removal deserve mention. Chlorine is more readily absorbed by alkalies than is chlorine dioxide, and if a mixture containing approximately equal amounts of the dioxide and chlorine is passed through a tube containing sodium hydroxide and the minimum of water (e.g. 6 g.-mol. NaOH in 20 ml. H_2O), chlorine dioxide of 99·7% purity is obtained.[79]

The oxides, hydroxides or carbonates of magnesium and calcium are also useful for this purpose.[13,79-83] The reaction can be made to form part of a reaction cycle if the product of absorption by (say) lime is further chlorinated to give calcium chlorate; this on treatment with hydrochloric acid will yield further quantities of chlorine dioxide-chlorine mixture.[82,83] The chlorine may also be removed by preferential solution in water,[14] or in sulphuric acid, when the chlorine dioxide dissolves in the acid and is readily recovered,[84] or by bringing the mixed gases into contact with water and sulphur, with which the chlorine reacts to give sulphuric and hydrochloric acids.[12] Precipitated gold in water will also separate chlorine from chlorine dioxide.[85]

In both laboratory and industrial processes for production of chlorine dioxide, safety precautions must continually be observed. Danger of explosion is minimized by keeping reaction temperatures as low as possible, eliminating contamination by organic matter, diluting gas and solid reactants with suitable inert materials, and using the chlorine dioxide as soon as possible after preparation.[86,87] Even so, the explosion of chlorine dioxide is often quite unpredictable.[88,89] In spite of this, it finds wide use as a bleach for flour, textiles, fats and oils, and in water purification.

PROPERTIES OF CHLORINE DIOXIDE

Physical Properties.

Chlorine dioxide is a yellow-orange gas, which liquefies to an orange-red liquid at 11°, and freezes at −59° to a solid which is usually likened to potassium dichromate in appearance.[72] The vapour pressures of chlorine dioxide over the liquid range are given in Table VI.

TABLE VI. - VAPOUR PRESSURE OF CHLORINE DIOXIDE

T°K.	p mm.	T°K.	p mm.
206	7	278·3	608
214(m.p.)	10	279·9	642
223	24	281	674
232·5	47	282	700
243·5	88	283	732
255	201	284(b.p.)	760
273	490		

From these data, the heat of vaporization of liquid chlorine dioxide is 6520 g.-cal./mol., and the Trouton constant is 23.[72] There is no evidence for any association in the liquid or in solution. The vapour density of the gas is normal, so that the compound is represented by the formula ClO_2 in all states. The density has been determined by the balancing column and pyknometer methods; the mean of five values is 1·642 g./c.c. at 0°.[94] The surface tension is 33·1 dynes/cm. at 0°, and the temperature coefficient is consistent with that expected for a non-associated liquid. The parachor is 98·7 units.[94] The high solubility of chlorine dioxide in water, and the formation of the hydrate $ClO_2,8H_2O$, have previously been referred to (Mellor,II,290). The distribution coefficient between carbon tetrachloride and water, given in Table VII is almost independent of concentration.[91]

These distribution coefficients are only slightly increased by the addition of sulphuric acid, potassium chlorate or potassium chloride to the aqueous solution. The freezing points of the aqueous solution[91] support the belief that the dioxide is not associated in water, and the constancy of the distribution coefficient shows that the dioxide is monomeric in carbon tetrachloride also. The value of the ratio $[ClO_2]_{\text{in } CCl_4}/[ClO_2]_{\text{in air}}$ is 50·7, compared with 34·3 for the water-air system.[92,93] The heat of solution of chlorine dioxide in

TABLE VII. - DISTRIBUTION COEFFICIENT OF CHLORINE DIOXIDE BETWEEN CARBON TETRACHLORIDE AND WATER

Molar Concentration in aqueous phase		Distribution Coefficient C_{CCl_4}/C_{H_2O}	
0°	25°	0°	25°
0·0016	0·003	1·17	1·60
0·006	0·007	1·174	1·61
0·010	0·029	1·180	1·63
0·033	0·035	1·210	1·66
0·060	0·057	1·224	1·65
0·122	0·103	1·268	1·67
0·164	0·121	1·270	1·69

water is 6600 ± 200 g.-cal./mol., and this value is independent of the concentration of the solution produced.[96] The heat of decomposition, determined by direct measurement of the heat of explosion in a calorimeter, was found to be 23500 g.-cal./mol. Similar determinations, with more consistent individual results, gave a value of 26585 ± 390 g.-cal./mol.[95] Because chlorine dioxide is more liable to detonate, it was necessary to work at much lower pressures (250 mm.) in the explosion chamber than in corresponding experiments with chlorine monoxide.[98]

The dielectric constant (ϵ) of solid chlorine dioxide has been determined by immersing the solid in a liquid which fills the space between the plates of a condenser; the composition of the liquid is varied until the immersed solid causes no change in the capacity, when ϵ for the solid is the same as ϵ for the liquid. By this method, ϵ for solid chlorine dioxide is 7·0.[110] Table VIII gives ϵ-values for solutions of chlorine dioxide.[111]

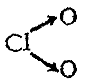
TABLE VIII. - DIELECTRIC CONSTANT OF DILUTE SOLUTIONS OF CHLORINE DIOXIDE IN CARBON TETRACHLORIDE

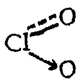
Temp. °C.	Mol. fraction chlorine dioxide				Molar Polarization c.c.
	0·000887	0·0024	0·00401	0·00739	
−18	ϵ = 2·3162	2·3230	2·3305	2·3457	79·8
−8	2·2958	2·3022	2·3092	2·3235	76·8
3	2·2736	2·2796	2·2860	2·2996	74·2
14	2·2514	2·2570	2·2630	2·2758	71·8
24	2·2313	2·2367	2·2422	2·2545	69·8

From these results, the dipole moment of chlorine dioxide is $1{\cdot}69 \pm 0{\cdot}09 \times 10^{-18}$ e.s.u., (about twice the value for chlorine monoxide), and the molecule is probably bent.[111] Having an odd number of electrons, it is an 'odd' molecule, and is paramagnetic, its molal susceptibility being 1310×10^{-6},[108,109] near that for nitrogen dioxide, also an odd molecule. The odd electron also permits the existence of a number of resonance forms. A decision on the actual structure to be attributed to the molecule depends largely on the molecular dimensions, measured by electron diffraction in gaseous chlorine dioxide, which are given below:-

	refs. 97–99	ref. 100
Cl–O distance, A.	1·53 ± 0·08	1·491 ± 0·014
O–Cl–O angle	137°	116·5 ± 2·5°

Some possible structures for the molecule are:-


I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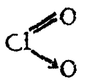
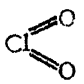

III


IV

and to these the various resonance forms should also be added. The sum of the single bond radii of Cl and O is 1·65, so that there is more multiplicity in the bond than is represented by I. The mean of the single and double bond radii is 1·57, and if the bond length of 1·53 is accepted, the 3-electron bond structure II, and structure III, are possible. However, more comprehensive examination of the electron diffraction photographs[100] led to the smaller value 1·491 for the Cl–O bond length, and if the value of 1·48 for the theoretical Cl=O distance is true, then the molecule must contain two double bonds (structure IV). In this case, the structure of chlorine dioxide would closely resemble that of sulphur dioxide.[100] The bond energy of the normal two-electron Cl–O bond has been calculated as 52 ± 1 kg.-cal., and the strengthening effect of the odd electron in ClO_2 as 15 kg.-cal.[101]

The absorption spectrum of chlorine dioxide (see page 651) is exceedingly complex. It consists of sequences of bands which occur at regular intervals, and forms an interesting example of absorption by a triatomic molecule.[102-107]

Thermal and Photo-decomposition.

The action of light on gaseous chlorine dioxide produces an initial decrease in pressure. A red liquid is formed on the walls of the vessel, and this becomes colourless on continued exposure. The decomposition cannot therefore be represented by the simple equation, $2ClO_2 \rightarrow Cl_2 + 2O_2$. Early experiments indicated that chlorine dioxide prepared in darkness and diluted with an equal volume of carbon dioxide remained stable for periods of several hours at temperatures above 85°, but exposure to the light from an electric lamp for a few seconds initiated decomposition. Chlorine monoxide catalyzes the decomposition of the dioxide, for the decomposition rate obtained with the illuminated gas can be reproduced in unilluminated chlorine dioxide by the addition of a little chlorine monoxide.[112] Because of its unique character, this photodecomposition has been much studied. In the dry gaseous state, the decrease in pressure on illumination has been shown to be due to the formation of chlorine trioxide, which separates as a red liquid.[113] One molecule of Cl_2O_6 is believed to be formed for each quantum absorbed.[114] On continuing the reaction, the pressure increases again, owing to the decomposition of the trioxide; and when the pressure change ceases the decomposition into chlorine and oxygen is complete. The final pressure rise resembles that obtained with chlorine-ozone mixtures.[113]

The spectrum of chlorine dioxide indicates that there is a region of predissociation below 3750 A. This may be related to the observation that chlorine dioxide does not absorb light at 5460 A., and that no photo-reaction occurs on exposing the dioxide to light of this wave-length produced by a mercury arc and glass filter.[115] However, the quantum efficiency at 4360 A. is only slightly less than at 3650 A. In view of the predissociation limit, light of wave-length 3650 A. has been used in the study of the influence of temperature on photodecomposition in the dry gas.[116] At 17°, the pressure falls on illumination, at first rapidly then slowly. The pressure then passes through a minimum and rises at an increasing rate until all the chlorine dioxide is decomposed. At this low temperature the chlorine trioxide is relatively stable and condenses on the walls. At 31°, with chlorine dioxide concentrations of up to 8%, there is an induction period of about six minutes during which there is little pressure change. The pressure then increases, rapidly and uniformly. Using 3650 A., and 3% chlorine dioxide, the rate of pressure increase indicates a quantum yield of 12, and the decomposition is probably a chain reaction. At this higher temperature, thermal decomposition of chlorine trioxide is more rapid, only a slight concentration of the trioxide is built up, and the reaction proceeds without appreciable decrease in pressure. The processes taking place on illumination at 3650 A. are probably as follows:-[114,116]

$$\begin{aligned} ClO_2 + h\nu &\rightarrow ClO + O \\ ClO_2 + O &\rightarrow ClO_3 \\ ClO + ClO &\rightarrow Cl_2 + O_2 \\ 2ClO_3 &\rightarrow Cl_2O_6 \ldots\ldots\ldots\ldots (a) \\ 2ClO_3 &\rightarrow Cl_2 + 3O_2 \ldots\ldots\ldots\ldots (b) \end{aligned}$$

Since stage (*b*) has a high heat of activation, more chlorine trioxide (*a*) is formed at lower temperatures.[114]

The photodecomposition of the moist gas is found to be more regular because of the removal of active groups by the water.[116] Quantum efficiencies have been compared at two wave-lengths; they are 3·7 at 3650 A. and 3·1 at 4360 A. The rate of decomposition is proportional to the intensity of light for chlorine dioxide concentrations up to 8%. Under moist conditions no chlorine is formed, and one molecule disappears from the gaseous phase for each molecule of chlorine dioxide decomposed. The initial steps in the decomposition depend upon wave-length.[116] Since 3650 A. is in the predissociation region, the first step must again be:-

$$ClO_2 + h\nu \rightarrow ClO + O$$

which may be followed by:-

$$\begin{aligned} ClO_2 + O &\rightarrow ClO_3 \\ 2ClO_3 &\rightarrow Cl_2O_6 \\ Cl_2O_6 + H_2O &\rightarrow HClO_3 + HClO_4 \\ ClO + ClO_2 &\rightarrow Cl_2O_3 \\ Cl_2O_3 + H_2O &\rightarrow 2HClO_2 \rightarrow HClO + HClO_3. \end{aligned}$$

The wave-length 4360 A. is in the band region, and the primary reaction will result in the formation of an activated molecule: $ClO_2 + h\nu \rightarrow ClO_2^*$. The initial step in the above scheme may then be replaced by:-

$$ClO_2^* \rightarrow ClO + O,^{116}$$

or by:-

$$ClO_2^* + ClO_2 \rightarrow ClO_3 + ClO.^{104}$$

The above scheme is in substantial agreement with the experimental evidence. The quantum yield is 3, independent of concentration and light intensity, and each of the acids HClO, $HClO_2$, $HClO_3$ and $HClO_4$ is found in the reaction 'mist' produced by moist decomposition.

Although chlorine dioxide does not absorb at 5460 A., a sensitized reaction takes place at this wave-length on the addition of bromine.[115,116] The sensitized decomposition takes place in the wet and the dry gas (and in carbon tetrachloride solution), and appears to resemble the direct decomposition at the lower wave-lengths; the quantum efficiency is the same as that for 3650 A. This is explained if the initial steps are:-

$$\begin{aligned} Br_2 + h\nu &\rightarrow Br_2^* \\ Br_2^* + ClO_2 &\rightarrow Br_2 + ClO_2^* \\ ClO_2^* + ClO_2 &\rightarrow ClO_3 + ClO \end{aligned}$$

and then as in the above scheme.

Photodecomposition of chlorine dioxide in carbon tetrachloride resembles in many respects that in the gaseous state. Early experiments showed that under the influence of violet light the decomposition approximately followed the law of photochemical equivalence.[117] The quantum efficiency is near 2 for a mean wave-length of 4150 A.,[118] but depends upon the wave-length of the light. At 4360 A. it is 1,[119,120] increasing to 2 for wave-lengths of 4050 A. and shorter;[119] at 3650 A. it is 1.[120] As in the gaseous state, chlorine and oxygen are not the only products of photodecomposition. At wave-lengths of 3650 and 4360 A., the oxides Cl_2O, Cl_2O_6 and Cl_2O_7 are also formed;[120] chlorine trioxide is formed in largest amount, and corresponds in some cases to as much as 20% of the chlorine dioxide decomposed.[121] The formation of these oxides in addition to chlorine and oxygen suggests that the mechanism of photodecomposition in carbon tetrachloride solution may be similar to that in the gas. Decomposition at 5460 A. may be sensitized by bromine. The quantity of chlorine trioxide formed is approximately the same as, but the amount of chlorine monoxide is less than, in the unsensitized reaction. The quantum yield for the sensitized reaction is 0·2 to 0·3; it depends on the light intensity but is independent of the concentration of chlorine dioxide.[120] Photodecomposition also occurs in solution in water, in which chlorine dioxide is very soluble. The quantum efficiency again increases with decreasing wave-length, from 0·2 at 4360 A. to 1·0 at 3000 A.[119] The scheme of photodecomposition will resemble that given above for moist chlorine dioxide, except that it is supposed that in aqueous solution the water intervenes to prevent further reaction of ClO with excess of chlorine dioxide. In solution, predissociation of chlorine dioxide occurs at lower energy values than as a gas; the initial step is therefore undoubtedly:-

$$ClO_2 + h\nu \rightarrow ClO + O.$$

The ClO is considered to react with water giving an intermediate product H_2ClO_2:-

$$ClO + H_2O \rightarrow H_2ClO_2$$
$$H_2ClO_2 + ClO \rightarrow HCl + HClO_3.$$

The decomposition products contain some chlorine and $HClO_2$, but consist predominantly of HCl and $HClO_3$, in amounts consistent with the above hypothesis.[119] The rate of decomposition in aqueous solution is proportional to the light intensity.

A study has been made of the role played by light in the explosion of chlorine dioxide. A quartz tube containing the gas was attached to a spectrograph, and the gas exploded by an electric spark. A continuous emission spectrum was obtained, with a maximum near 4740 A. This maximum is attributed to recombination of the atoms $2Cl \rightarrow Cl_2 + h\nu$, and $2O \rightarrow O_2 + h\nu$, the released energy being non-quantized.[122]

In the absence of light, chlorine dioxide undergoes thermal decomposition at a rate which increases considerably with increase in temperature.[123] The nature of the walls, and the area/volume ratio of the containing vessel, have a pronounced influence on decomposition rate, so that the decomposition is regarded as a chain reaction which starts on the vessel walls. The temperature coefficient differs from vessel to vessel; at 40° in a glass flask it is 5 for a 10° rise in temperature. The primary step in the reaction is again $ClO_2 \rightarrow ClO + O$. Chlorine trioxide is postulated as an intermediate product which may take part in chain propagation, but in reactions such as $ClO_3 + ClO_2 \rightarrow ClO_2 + 2O_2$ may serve to break the chains. At temperatures between 35° and 55°, the decomposition rate is proportional to the square root of the partial pressure of chlorine dioxide, and to the first power of the total pressure. If the reaction velocity exceeds a certain limit (which varies with the containing vessel) these rules no longer hold; the decomposition rate increases continuously and an explosion results.[123] The addition of oxygen, chlorine or carbon dioxide increases the decomposition rate merely because they increase the total pressure. Carbon monoxide retards the reaction, presumably by breaking chains involving the oxygen atoms produced on primary dissociation. Addition of chlorine monoxide in about equal quantity also retards the reaction. A chain-breaking mechanism is probably again involved, since some of the chlorine monoxide is itself decomposed. This observation is in contrast to the effect produced in solutions; the decomposition of chlorine dioxide in the absence of light and in carbon tetrachloride solution is catalyzed by traces of chlorine monoxide of the order of 0·001 mol./litre.[93] Unstable solutions (in which no attempt to remove the chlorine monoxide impurity was made) decomposed slowly in the dark, with a half-life period of about 30 hours at room temperature.[92] The decomposition under these conditions has been followed kinetically and found to be represented by the equation $-d[ClO_2]/dt = k[ClO_2]^{4/3}[Cl_2O]^{1/3}$. The chlorine monoxide may be removed by treating the solution with barium hydroxide, ($Ba(OH)_2,8H_2O$), when the solution becomes relatively stable. The chlorine monoxide induces the dark reaction, and itself results from exposure of the solution to light. Thus, if a solution is stabilized by baryta treatment and then exposed to light for a short time before being placed in the dark, the decomposition rate is similar to that of the unstabilized solution.[92]

Chemical Properties.

The chemical reactions of chlorine dioxide have been little studied in recent years despite the interest in the physical properties, and the account previously given (Mellor,II,289), still covers the major part of its chemistry. In aqueous solution at low temperatures it reacts with water very slowly, and can be expelled again from the solution even after long standing. In light its solution slowly gives hydrochloric and chloric acids. In alkaline solution it behaves as a mixed anhydride, and slowly forms chlorite and chlorate; in the presence of a reducing agent the formation of chlorate can be prevented. Since both chlorine dioxide and chlorites are of value for bleaching purposes, these reactions are treated in more detail under the chemistry of chlorites. The reversible process $ClO_2 + e^- \rightleftharpoons ClO_2^-$ is of interest in this connexion, and has an equilibrium oxidation potential of 0·950 V. as measured with a normal hydrogen electrode.[124] A mixture of hypochlorous acid and chlorine dioxide has some advantages in certain bleaching processes.[125] These two compounds undergo mutual reduction, and the kinetics of the reaction have been studied. The rate of decomposition of chlorine dioxide is given by:-

$$-d[ClO_2]/dt = k_1[HOCl][ClO_2] + k_2[ClO_2]^2$$

where both k_1 and k_2 are functions of the hydrogen ion concentration in solution.[126]

Although investigations of purely chemical interest are limited, a considerable amount of work has been carried out on the bactericidal, and particularly the bleaching powers of chlorine dioxide.[90] Notable among these are its uses in water disinfection,[127-141] the sterilization of spices[142] and fish,[143] and the bleaching of oils, fats and waxes,[144-146] flour,[147-153] pectin-containing material,[154] alginic acid,[155] textiles,[156] and woodpulp.[157-161]

Percarbonates and perborates react with chlorine dioxide to give chlorites;[162] persulphates do not react, and are used in the preparation of chlorine dioxide. With hydrogen peroxide in the presence of precipitated calcium carbonate, chlorine dioxide reacts quantitatively to give the chlorite,[162] though under different conditions the equilibrium may be used in the reverse direction for the preparation of chlorine dioxide. The addition of sodamide to a solution of chlorine dioxide in carbon tetrachloride gives sodium amidochlorate;[163] this gives a precipitate with silver nitrate which is insoluble in acetic acid, and may be the compound $Na^+[NH_2ClO_2]^-$. Reaction with fluorine gives the interesting addition compound ClO_2F.[164] At 20° mixtures of the two gases explode, the chlorine dioxide decomposing to chlorine and oxygen. This explosion is not prevented by low temperature alone, or by slight dilution of the gas mixture with an inert gas (e.g. nitrogen). However, when the gases are mixed at 0° at partial pressures of 25·6 mm. ClO_2, 54·0 mm. F_2, and 540 mm. air, smooth reaction takes place within two minutes to produce the compound ClO_2F. This compound has m.p. −115°, b.p. about −6°; its Trouton constant is 23·2 and the heat of evaporation 6·2 kg.-cal./mol. The vapour pressure is 8·8 mm. at −78°, and 740 mm. at −6·3°. The compound is readily hydrolyzed, and fumes in moist air.[164] (See page 183).

Chlorine dioxide oxidizes elementary sulphur, and may do so explosively. The reaction products are mainly sulphur monochloride and sulphur dioxide. The reaction becomes slower in the presence of water, when sulphuric acid is formed.[165] Chlorine dioxide reacts with mixtures of sulphur with metal chlorates. The reaction is complicated, since the products of the ClO_2–S reaction, e.g. SO_2, also react explosively with the sulphur–chlorate mixture.[166] A reaction which merits further investigation is that between aqueous solutions of chlorine dioxide and metals.[167] Some metals dissolve to give chlorite in solution, and if chlorine dioxide behaves under these conditions as an electron acceptor, the process could involve simple electron transfer from the metal: $M + ClO_2 \rightarrow M^+ + ClO_2^-$. Using the metal in the form of dust to increase its surface area, and aqueous solutions containing 65 g./l. of chlorine dioxide at 0°, or 45 g./l. at 25°, the yields of chlorite with respect to the metal in solution were found to be 82–85% for zinc, and 81–91% for cadmium. Magnesium and aluminium also react in this manner. The reactions may also be carried out using acetic anhydride as reaction medium, but side-reactions occur and the yields of chlorite are lower (20% with zinc and 16% with magnesium). No reaction with powdered zinc or magnesium was observed using pure liquid chlorine dioxide.[167] Nickel filings react with chlorine-free chlorine dioxide in aqueous solution to give nickel chlorite in almost 100% yield at temperatures of 16° and 25°. If the reaction is carried out at higher temperatures (45°) the chlorite is unstable, and chloride and chlorate are the main products. The nickel chlorite is also unstable at lower temperatures if the chlorine dioxide used contains appreciable quantities of chlorine.[167]

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CHLORINE TRIOXIDE

This oxide was prepared, though not recognized, as early as 1843, as a brown liquid which separates on the walls of the vessel when chlorine dioxide is exposed to light.[1] An attempt was made to purify the material, and analysis gave an empirical formula Cl_6O_{17}. There appears to be little further mention of the compound until 1923,[2] and in 1925 a study of the photodecomposition of chlorine dioxide made it clear that at least one unknown chlorine oxide was formed as an intermediate product.[3] Chlorine trioxide was first identified as a product of this reaction. The red droplets formed during photodecomposition were purified by distillation at low pressure; elementary analysis showed the Cl:O ratio to be 1:3, and cryoscopic measurement (in carbon tetrachloride) showed the compound to have the dimeric form Cl_2O_6 (dichlorine hexoxide).[4] The compound as first isolated probably contained small quantities of other oxides in solution, since its physical properties were not quite in accord with accepted modern values. (See Table X, page 538). The postulated mechanisms for its formation by this method have been discussed under the photodecomposition of chlorine dioxide. Chlorine trioxide is also prepared by the action of ozone on chlorine or, preferably, on chlorine dioxide. These reactions, with such properties of chlorine trioxide as influence the reactions, will be discussed together.

A kinetic study of the chlorine-sensitized decomposition of ozone revealed that the pressure changes following the mixing of chlorine and oxygen were very irregular, and the nature of this irregularity indicated that several component reactions were probably taking place.[5] When the gas mixture was illuminated by blue light, there was a general decrease in reaction rate with time of illumination.[5,6] Also, on freezing out all other gases with liquid air, the quantity of oxygen produced in the reaction proved to be appreciably greater than the amount which the pressure increase would suggest. Another reaction therefore takes place which causes a decrease in pressure, and this decrease was largely explained when chlorine trioxide was identified on the walls of the vessel.[6] A more detailed examination of the oxygen discrepancy led to the identification of dichlorine heptoxide, Cl_2O_7, as an additional product of reaction. Using chlorine and ozone pressures of 60 – 70 cm. (pressure being measured in cm. of sulphuric acid, d 1·84) separation of trioxide was plentiful at 0°, and was still observed at 20°. For the study of the part played by chlorine trioxide in the chlorine-ozone reaction, the trioxide could be conveniently prepared as required by illuminating the gas mixture in the reaction vessel; excess gases were pumped off, and any impurity was removed by alternately freezing and liquefying the trioxide while evacuating the vessel.[7]

The reaction is suitably accounted for by the following steps:-[8]

$$\begin{gathered} O_3 + h\nu \rightarrow O_3^* \\ O_3^* + Cl_2 \rightarrow ClO + ClO_2 \\ ClO_2 + O_3 \rightarrow ClO_3 + O_2 \\ 2ClO \rightarrow Cl_2 + O_2. \end{gathered}$$

The close relationship between the ClO radical and ClO_3 has also been emphasized.[16] These reactions cannot, however, be examined as a separate sequence, since the chlorine trioxide produced also reacts with ozone. This reaction probably has a chain mechanism, represented by the steps:-[7]

$$\begin{gathered} ClO_3 + O_3 \rightarrow ClO_2 + 2O_2 \\ ClO_2 + O_3 \rightarrow ClO_3^* + O_2 \\ ClO_3^* + O_3 \rightarrow ClO_2 + 2O_2 \end{gathered}$$

and so on; ClO_3^* represents an energy-rich molecule. The initial rate of this reaction is proportional to the ozone pressure, but the rate decreases as the reaction proceeds, since the oxygen produced has an inhibitory effect. The rate is expressed by the equation:-

$$dp/dt = k[O_3] + k_1[O_2]/[O_3],$$

where p is the gas pressure. Added nitrogen or chlorine has the same inhibitory effect. The ratio of the specific rate constants at 20° and at 0° is 3·92, which corresponds with a heat of activation of 10·9 kg.-cal./mol.[7]

In addition to its direct reaction with ozone, the thermal decomposition and the chlorine-sensitized photochemical decomposition of chlorine trioxide also play significant roles in the chlorine-oxygen reaction, e.g. by terminating reaction chains such as those discussed above. There are two modes of thermal decomposition:-

$$2ClO_3 \rightarrow Cl_2 + 3O_2 \qquad (1)$$

$$\text{and } 2ClO_3 \rightarrow 2ClO_2 + O_2 \qquad (2)$$

To determine the relative extents to which these two reactions occur, about 0·5 ml. of liquid chlorine trioxide was sealed in a reaction vessel, and the pressure changes observed in the temperature range 0° – 30°. Increase in pressure (Δp) was noted, all gases other than oxygen were then frozen out by liquid air, and the pressure due to oxygen alone (pO_2) was measured. Assuming reaction (1), the ratio $pO_2/\Delta p$ should be 0·75; for reaction (2), the ratio is 0·33. Some experimental values of the ratio are given in Table IX;[6] these are each the mean of several determinations.

It is evident that at the two lower temperatures, decomposition into chlorine dioxide and oxygen occurs. At 30°, decomposition appears to occur in both ways (1) and (2) to approximately the same extent, although initial decomposition may be by equation (2) at all temperatures, followed by further decomposition of the dioxide at the higher temperatures.

TABLE IX.- THERMAL DECOMPOSITION OF CHLORINE TRIOXIDE

Temp. °C.	$pO_2/\Delta p$
0	0·34
10	0·38
20	0·40
30	0·50

There is direct evidence also for the formation of chlorine dioxide by thermal decomposition of the trioxide. When a drop of the liquid trioxide is sealed in a tube and immersed in a hot water bath, the colour rapidly changes to the yellow-green of chlorine dioxide, then diminishes rapidly. The dioxide was identified spectroscopically.[4,10]

The heat of activation for the decomposition of liquid trioxide has been calculated from the Arrhenius equation, assuming that the velocity constant for the reaction is proportional to the rate of pressure increase. From pressure-time curves over the temperature range 5°–15°, the temperature coefficient is 3·8 per 10° rise in temperature, and the heat of activation 22 ± 2 kg.-cal.[10] A separate study of the temperature coefficient confirms the above value, and gives 21 to 26 kg.-cal for the heat of activation of the reaction $ClO_3 \rightarrow ClO_2 + \frac{1}{2}O_2$.[5,10] For the ultimate thermal decomposition, $ClO_3 \rightarrow \frac{1}{2}Cl_2 + \frac{3}{2}O_2$, the heat of decomposition, measured by a calorimetric technique, is −37 ± 2 kg.-cal.[12]

The photochemical decomposition of chlorine trioxide is sensitized by chlorine. Illumination of the trioxide vapour in equilibrium with the liquid does not affect the decomposition rate appreciably, but when chlorine is added, illumination by blue light accelerates the rate of pressure increase. At high light intensity, the $pO_2/\Delta p$ ratio is nearly 0·75, so that the decomposition products are chlorine and oxygen.[6]

It is clear from the above discussion that chlorine dioxide and ozone will react to form chlorine trioxide; in fact the reaction $ClO_2 + O_3 \rightarrow ClO_3 + O_2$ affords the best method of preparation.[9,10] The reaction can be suitably controlled by mixing a stream of ozonized oxygen with a stream of oxygen containing chlorine dioxide. Oxygen gas from a cylinder is passed through an ozonizer to give an ozone concentration of about 7% by volume. A separate stream of oxygen is passed over chlorine dioxide to give a gas mixture containing about 20% by volume of the dioxide. The two gas streams are mixed (20 litres/hour for the ozone stream and 2 litres/hour for the chlorine dioxide stream) in a reaction chamber cooled by melting ice, where the trioxide condenses. The product at this stage contains as impurities chlorine dioxide and dichlorine heptoxide. In subsequent purification it is necessary to avoid the use of taps, since the trioxide attacks tap grease. Very pure samples of the trioxide cannot be obtained by distilling away the top fractions, since this does not remove involatile impurities, which probably result from reaction with the glass vessels. The oxide may be purified by fractional distillation; the reaction reservoir is kept at 6° and the pure trioxide collected in a cold trap at −20°.

Some physical properties of chlorine trioxide are listed below: its ready thermal decomposition makes the determination of physical properties difficult. For example, three samples gave consistent melting points of 3·50°, 3·52° and 3·50°, but on keeping a sample for 15 minutes at 5·5° the melting point fell by 0·2°, and on keeping for 7 minutes at 17° there was a further decrease of 0·45°.

TABLE X. - PHYSICAL PROPERTIES OF CHLORINE TRIOXIDE

Melting point	+3·5°
Boiling point	+203°
Colour	Dark red liquid Orange-red solid at -78° Yellow solid at -180°
Density g./c.c. at 3·5°	2·023 ± 0·003
Molecular volume, c.c.	82·7
Coefficient of expansion c.c./c.c./deg.	$12 \pm 3 \times 10^{-4}$
Trouton's Constant	21
Latent heat of evaporation, kg.-cal./mol.	9·5 ± 1
Latent heat of sublimation, kg.-cal./mol.	12·3 ± 0·5

Chlorine trioxide has a higher density, melting point, and latent heat of evaporation than any other oxide of chlorine. Several determinations of the vapour pressure have given values of the order of 1 mm. at room temperature.[4,7,9,13] Using small quantities of trioxide of high purity, it has been possible to determine values for the vapour pressure accurate to 0·02 mm. for temperatures below 0°. At higher temperatures the possible error is increased owing to thermal decomposition. When the logarithm of the pressure is plotted against $1/T$, the results for solid and liquid lie on two straight lines represented by the equations:-

$$\log_{10} p(\text{mm.}) = -2070/T + 7{\cdot}1 \qquad \text{(liquid)}$$
$$\log_{10} p(\text{mm.}) = -2690/T + 9{\cdot}3 \qquad \text{(solid)}$$

These values cover the temperature range -40° to 20°; the vapour pressure is 0·31 mm. at 0°.[10]

Molecular Constitution.

Chlorine trioxide can exist either in the monomeric (ClO_3) or dimeric (Cl_2O_6) form, and the position of the equilibrium $2ClO_3 \rightleftharpoons Cl_2O_6$ depends upon physical conditions. In the gaseous state the oxide is entirely in the monomeric form.[14] A sample of the gaseous oxide was sealed into a quartz tube fitted with a pressure gauge and end windows, and the vapour pressure and absorption spectrum recorded simultaneously while increasing the temperature. At room temperature the continuous absorption due to ClO_3 decreased with time, and the band absorption of chlorine dioxide increased. The tube was then heated until no further pressure change occurred. If chlorine trioxide exists in the monomeric form the total decomposition $ClO_3 \rightarrow \frac{1}{2}Cl_2 + \frac{3}{2}O_2$ implies a two-fold increase in pressure: the ratios of initial to final pressure observed were 2·03, 1·97, 2·04 and 1·95.[10] In solution in carbon tetrachloride the oxide is almost entirely dimerized to Cl_2O_6. The molecular weight, determined by cryoscopic measurements on the solutions, has been found to be only slightly less (153, 156) than the value for the dimer (167).[5,15] In the liquid and solid states, dimerization is virtually complete. This is consistent with the low vapour pressure of both liquid and solid. The position of equilibrium has been determined in an elegant manner by measuring the magnetic susceptibility of dichlorine hexoxide by the Guoy method over the temperature range -40° to +10°.[11] Because of its odd number of electrons, the molecule ClO_3 will be paramagnetic, whereas the dimer Cl_2O_6 should be diamagnetic. (The system is closely similar to $2NO_2 \rightleftharpoons N_2O_4$). Some results are given in Table XI and they show clearly that in the solid and liquid states the oxide exists almost entirely as dichlorine hexoxide. The experimental

TABLE XI. - MAGNETIC SUSCEPTIBILITY OF DICHLORINE HEXOXIDE

Temp. °C.	Mass susceptibilities × 10^6			ClO_3 content %	$K_c \times 10^3$
	ClO_3 (calc.)	Cl_2O_6 (calc.)	Observed values		
-40	19·15	-0·405	-0·264	0·721	2·54
-30	18·36	-0·405	-0·259	0·775	2·94
-20	17·64	-0·405	-0·255	0·826	3·34
-10	16·98	-0·405	-0·251	0·886	3·85
0	16·36	-0·405	-0·247	0·943	4·36
10	15·79	-0·405	-0·243	1·001	4·91

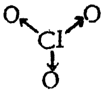
values for the diamagnetism are a little less than the calculated value for Cl_2O_6. If this difference is due to the presence of ClO_3 molecules, then the content of this species is given in column 5. It is to be expected that dissociation of the dimer would increase with increasing temperature; on the other hand, thermal dissociation increases similarly, and since the chlorine dioxide so produced would also be paramagnetic, the values in column 5 are maximum values. The last column shows the equilibrium constant for the dissociation, concentrations being expressed in g. mol./litre. When $\log_{10}K_c$ is plotted against $1/T$, a straight line is obtained, represented by the equation:-

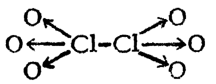
$$\log_{10}K_c = -0{\cdot}974 - 1730/2{\cdot}3\,RT.$$

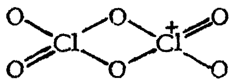
It follows that the heat of dissociation $Cl_2O_6 \rightarrow 2ClO_3$ is 1730 ± 500 g.-cal./g.mol. No break in the line occurred at the melting point.[11] This small heat of dissociation no doubt accounts for the fact that the constant in the vapour pressure equation for the liquid (see above) has the normal value according to Trouton's rule, in spite of the association to hexoxide.[10]

Structure.

No direct evidence is yet available on the structure of either of the molecules ClO_3 or Cl_2O_6. There is no doubt that chlorine trioxide contains three Cl-O bonds, and no peroxy-link, but whether the structure is planar or pyramidal is a matter for conjecture. The ion ClO_3 is pyramidal. The addition of an extra electron to ClO_3 forms an electron pair to occupy the fourth apex of a tetrahedron, but without this extra electron the ClO_3 molecule may be nearly planar. Two structures appear possible for the dimer:-




(I)


(II)

The odd electrons in each ClO_3 unit may be paired to give a direct Cl-Cl bond, as in structure (I). This structure puts electric charges of the same sign on two adjacent (chlorine) atoms, and thus contravenes the adjacent charge rule.[17] This is not a serious objection, since the corresponding structure for dinitrogen tetroxide has been confirmed by crystallographic analysis. In view of the small heat of dissociation this bond must be extremely weak, and structure (II) presents an attractive alternative mode of association. The oxygen atoms are considered as being tetrahedrally disposed round each chlorine atom.[18]

The chemical reactions of chlorine trioxide have been little investigated. It is the least explosive of all the oxides of chlorine and does not explode with shock or sudden heat. It is a very strong oxidizing agent, and will react violently (even explosively) with stopcock grease, wood, alcohol and in fact most forms of organic matter.[4] There appear to be no really safe conditions under which this and the other oxides of chlorine can be handled. It is stated that 'elaborate precautions against harm arising from explosions have only partly succeeded in preventing personal injuries'.[10] The oxide reacts vigorously (and may explode) with water, the main products being chloric and perchloric acids:-[4]

$$Cl_2O_6 + H_2O \rightarrow HClO_3 + HClO_4.$$

When the gas is mixed with water vapour, crystals of perchloric acid hydrate, $HClO_4,H_2O$, separate on cooling. With alkali, a mixture of chlorate and perchlorate is formed.

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DICHLORINE HEPTOXIDE

This oxide is the true anhydride of perchloric acid ($Cl_2O_7 + H_2O \rightleftharpoons 2HClO_4$), and it was first isolated by dehydrating the acid.[1] Anhydrous perchloric acid was added slowly to phosphoric oxide below -10°, and after a day the dichlorine heptoxide was distilled off. There have been various modifications of this technique, many designed to minimize the danger of explosion. When the heptoxide was prepared by adding phosphoric oxide to cooled 70% perchloric acid, the yield was small, and 'small nerve-racking explosions' occurred during the process. To avoid this, the 70% perchloric acid may be absorbed in 3-4 times its weight of purified kieselguhr, and mixed with phosphoric oxide in an equal weight of kieselguhr.[2] The heptoxide is distilled off at 80°-90°, and a pressure of 0·2 mm. Other dehydrating agents may be used. A mixture of potassium perchlorate (3 parts) and chlorosulphonic acid (5 parts) was cooled in an ether-solid carbon dioxide bath, and distilled under the vacuum from a water pump. On gradually raising the temperature to 70°-75° a yellow oily liquid was obtained containing dichlorine heptoxide together with other chlorine oxides and sulphuryl compounds. By redistillation, a 50% yield of 98-99% Cl_2O_7 was obtained.[2] However, where material of high purity is required, phosphoric oxide appears to be the best dehydrating agent. The heptoxide used for vapour pressure measurements[3] was prepared by first concentrating a 60% perchloric acid solution by distilling off water at low pressure.

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The concentrated acid was surrounded by a cooling bath of solid carbon dioxide and alcohol, and phosphoric oxide added slowly through a side tube. Keeping the pressure low under the pump, the mixture was warmed to 40°; dichlorine heproxide was evolved, and collected in a cold trap. After the first low pressure distillation, the liquid may be distilled at atmospheric pressure. It was distilled through phosphoric oxide tubes, passed over copper turnings to remove the last traces of chlorine and other chlorine oxides, and fractionated until a colourless sample was obtained. To minimize the risks from explosion, no more than 1 c.c. was prepared at one time.[3] Solutions of dichlorine heptoxide in carbon tetrachloride have been prepared directly by adding 82 g. of 70% aqueous perchloric acid drop by drop to a mixture of 120 c.c. of carbon tetrachloride and 50 g. of phosphoric oxide which is stirred rapidly. When the mixture is warmed and filtered, a 2·5% solution of the heptoxide is obtained. No phosgene is formed in the reaction, and the solution can be concentrated safely by redistillation.[2]

Dichlorine heptoxide is formed when chlorine and ozone react in blue light. This complicated reaction involves all the oxides of chlorine, but dichlorine heptoxide is relatively inert chemically and tends to remain unchanged once it is formed, whereas the other oxides undergo further reaction. The discrepancy between the quantity of oxygen produced and that indicated by the pressure change in a chlorine-ozone mixture is greater than can be accounted for by the formation and condensation of chlorine trioxide.[4] The product responsible for this additional discrepancy was shown to be the heptoxide by thermally decomposing the trioxide, and pumping off all chlorine and oxygen from the system: the vapour pressure of the drop of colourless liquid remaining was found to be identical with values determined for dichlorine heptoxide.[3,4] Its formation is believed to be due to reaction between chlorine trioxide and ozone, as follows:-[4]

$$\mathrm{ClO_3 + O_3 \rightarrow ClO_4 + O_2}$$
$$\mathrm{ClO_4 + ClO_3 \rightarrow Cl_2O_7}.$$

These reactions are additional to, and take place at the same time as, other $\mathrm{ClO_3}$-$\mathrm{O_3}$ reactions already discussed under chlorine trioxide.

Some physical properties are listed in Tables XII and XIII.

TABLE XII. - PHYSICAL PROPERTIES OF DICHLORINE HEPTOXIDE

Melting point °C.[3]	-91·5 ± 2
Boiling point °C.[3]	80 ± 1
Density at 0°C.[5]	1·86
Molecular volume c.c.	98·4
Trouton's constant[3]	23·4
Latent heat of evaporation kg.-cal./mol.[3]	8·29

TABLE XIII. - VAPOUR PRESSURE OF DICHLORINE HEPTOXIDE

Temp. °C.	*P* mm.	Temp. °C.	*P* mm.
-29	4·0	8	36·7
-21	7·0	14	48·9
-13·5	9·1	20·3	72·0
-8	14·1	28·5	93·6
0	23·7	30	108·0

The vapour pressure is related to the absolute temperature by the equation:-

$$\log_{10}P\ (\text{mm.}) = -1818/T + 8{\cdot}03.$$

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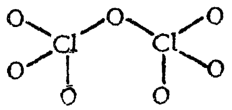
The latent heat was determined from this relation, and the boiling point by extrapolation of the vapour pressure curve. The heat of dissociation of gaseous dichlorine heptoxide has been measured by passing the gas continuously over a red hot platinum filament in a calorimeter. The gas decomposes into its elements ($Cl_2O_7 \rightarrow Cl_2 + 3\frac{1}{2}O_2$), and from the heat removed by the calorimeter and produced at the filament, the heat of decomposition was found to be 63·4 ± 3 kg.-cal./mol.[6]

Structure.

Evidence on structure is based largely on Raman spectrum measurements.[7] The spectrum of dichlorine heptoxide contains lines produced by the vibrations of the ClO_3 group. The dipole moment of the heptoxide, measured in solution in carbon tetrachloride at 20°, is 0·72 ± 0·02 Debye units. The Cl_2O_7 molecule can be considered to consist of two ClO_3 units connected by an oxygen bridge.



From the dipole moment, the angle Cl–O–Cl has been calculated to be 128°.[7] The molecule is, of course, non-planar. This large bond angle, resulting from steric repulsion of the O atoms in the ClO_3 groups, will cause strain in the molecule at this point. The normal 2-electron O–Cl bond energy is calculated as 52 kg.-cal., and there are six of these bonds in the molecule. The total bond energy is 402 kg.-cal./mol. so that steric repulsion weakens the molecule to the extent of 14 kg.-cal./mol.[8]

Dichlorine heptoxide is probably the most stable of the oxides of chlorine, and is inferior to the other oxides as an oxidizing agent. In the cold, it may be brought into contact with sulphur, phosphorus, paper and wood without explosion or reaction. It reacts slowly with water to form perchloric acid. Nevertheless, it still retains the explosive features of the chlorine oxides, and explodes violently under a blow or when heated rapidly. It undergoes slow thermal decomposition at room temperature.

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CHLORINE TETROXIDE

It has been claimed that the oxide ClO_4 is produced by reaction of silver perchlorate with iodine in anhydrous ether, the concentrations of the reactants being about 1%:-[1,2]

$$2AgClO_4 + I_2 \rightarrow 2AgI + 2ClO_4.$$

The presence of a small amount of an unstable iodo-compound was also observed.[1] The chlorine tetroxide was said to be colourless, not volatile in ether, and probably dimeric, $(ClO_4)_2$. It was believed to react with water[1] according to the following equation:-

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$$2ClO_4 + H_2O \rightarrow HClO_4 + HO.ClO_4.$$

It has also been regarded as an intermediate in the reaction between perchloric acid and fluorine.[3] The following facts are submitted as evidence that the solutions in ether contain chlorine tetroxide rather than perchloric acid:[1] (*a*) the solution liberated iodine from hydriodic acid, though not in equivalent amount; (*b*) with zinc and magnesium metals, perchlorates were produced and no hydrogen was evolved. (The reaction could thus be explained in terms of a simple electron transfer process: with iron, tin and copper, perchlorates of the metals in more than one valency state were produced, and with cadmium, bismuth and silver, reaction was slow and incomplete). (*c*) The reactions of solutions of perchloric acid and of ethyl perchlorate differed from those of the chlorine tetroxide solutions.

The evidence for the existence of this oxide was in no way conclusive, and an alternative interpretation of the experimental data has been proposed involving the intermediate formation of iodine perchlorate:-[4]

$$AgClO_4 + I_2 \rightarrow AgI + IClO_4;$$

followed by iodination of ether to give an unstable iodo-ether:-

$$C_2H_5.O.C_2H_5 + IClO_4 \rightarrow C_2H_5.O.C_2H_4I + HClO_4.$$

The iodo-ether slowly reacts with more silver perchlorate:-

$$AgClO_4 + C_2H_5.O.C_2H_4I \rightarrow AgI + C_2H_5.O.C_2H_4.ClO_4.$$

The overall reaction therefore leads to the formation of equivalent amounts of perchloric acid and the ether perchlorate. On this basis, the oxidizing power of the solution should vanish towards the end of the reaction, as the iodine perchlorate is consumed in iodinating the solvent. This has been found to be the case,[4] although the observation has been contested.[5] The second and third stages are difficult to confirm because of the instability of the iodinated ether, but receive support from later work. When silver perchlorate and iodine react in the presence of an aromatic compound C_6H_5X (e.g. chloro- or nitrobenzene) the reaction is exclusively:-

$$C_6H_5X + I_2 + AgClO_4 \rightarrow C_6H_5XI + AgI + HClO_4,$$

and there is no evidence of the formation of chlorine tetroxide. The aromatic iodo-compound is not affected by excess of silver perchlorate. However, alkyl iodides do react:-

$$C_2H_5I + AgClO_4 \rightarrow C_2H_5ClO_4 + AgI.$$

When iodine and silver perchlorate react in ether solution, the initial precipitation corresponds to 1 mol. of silver iodide per mol. of iodine. Reaction with the solvent is an essential step in the formation of the second molecule of silver iodide. This precipitation is slow, and during the process the oxidizing power of the solution disappears.[6] The original postulate that chlorine tetroxide was formed was based on the assumption that ether behaved as an inert solvent: since this appears to be untrue, there is no apparent justification for supposing that chlorine tetroxide is formed in the reaction between iodine and silver perchlorate.

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HYPOCHLOROUS ACID AND THE HYPOCHLORITES

Preparation of Hypochlorous Acid.

The preparative methods previously described (Mellor,II,244,276) remain the important methods, and recent developments have been concerned largely with the study of the mechanisms of these reactions, and of modifications in the experimental techniques. Hypochlorous acid may be prepared by dissolving its anhydride (chlorine monoxide) in water. By this method dilute solutions only are obtainable; the position of the equilibrium $Cl_2O + H_2O \rightleftharpoons HOCl$, and the solubility of chlorine monoxide in water, have already been discussed (see page 515). Hydrolysis of certain non-metal chlorides also gives hypochlorous acid provided that high temperatures are avoided; for example, $NCl_3 + 3H_2O \rightleftharpoons NH_3 + 3HOCl$. The formation of hypochlorous acid by reaction between chlorine and water is probably the most important method. In the gaseous state and at high temperatures the reaction is $Cl_2 + H_2O \rightarrow 2HCl + \frac{1}{2}O_2$, but in aqueous solutions chlorine reacts as follows: $Cl_2 + H_2O \rightarrow HCl + HOCl$.

The equilibrium constants K for this reaction, $K = [HOCl][H^+][Cl^-]/[Cl_2]$, have been determined from the aqueous solution/carbon tetrachloride distribution coefficient and from the electrical conductivity of the aqueous solutions. The values are given in Table XIV.[1]

TABLE XIV.- EQUILIBRIUM CONSTANTS FOR HYDROLYSIS OF CHLORINE

Temperature	0°	1·2°	15°	17·6°	25°	70°
$K \times 10^{-4}$	1·56	1·64	3·16	3·63	4·48	10·0

Thus at atmospheric pressure saturated chlorine water contains about 0·06 M. total chlorine, about half of which is free chlorine and half is hydrolyzed. The rate of reaction has been studied by the streaming method.[2] Hydrolysis is extremely rapid, being substantially complete within one second at 1°C.[3,4] An attempt to explain the kinetics of the reaction, assuming reaction between chlorine and water molecules:-

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-,$$

was only partially successful,[3] and it is more satisfactory to regard the process:-

$$Cl_2 + OH^- \rightleftharpoons HOCl + Cl^-$$

as the rate-determining reaction.[5]

Thus $d[Cl_2]/dt = k_1[Cl_2][OH^-] - k_2[HOCl][Cl^-]$ and $K = k_2/k_1k_w$. The value of the velocity constant k_1 is about 5×10^{14}, and the values at 17·6° are only slightly greater than those at 1·2°, so that the reaction requires little or no activation energy and would appear to occur at almost every collision. Reaction between a chlorine molecule and a hydroxyl ion involves an increase of 22 to 25 entropy units.[5]

The concentration of hypochlorous acid available by this method is limited by the low solubility of chlorine in water, but the yield may be increased by the addition of compounds which will remove the hydrochloric acid from solution. This is done in the usual laboratory method by passing chlorine into aqueous suspensions of mercuric oxide, but this gives solutions of hypochlorous acid containing dissolved mercury salts. The difficulty may be overcome by suspending mercuric oxide in carbon tetrachloride. The

Refs. p. 554

chlorine monoxide formed on treatment with chlorine dissolves in the carbon tetrachloride; when this solution is extracted with water, a pure solution of hypochlorous acid is obtained which contains no mercury salts and is practically free from chlorides. This process can give concentrated solutions which are very stable.[6] Suspensions of many other compounds in place of mercuric oxide have been used (Mellor,II,244), but many suffer from the same disadvantage in that the solution is contaminated with metal salts. However, an aqueous suspension of bismuth trioxide gives solutions of hypochlorous acid which are virtually bismuth-free:-

$$Bi_2O_3 + H_2O + Cl_2 \rightarrow 2BiOCl + 2HOCl$$

although high concentrations of the acid cannot thus be obtained.[6,7] On a large scale, hypochlorous acid may be produced in a continuous process by treating mercuric or silver oxide with chlorine so as to convert only part of the chlorine to chlorine monoxide. This gas mixture is treated with water under conditions such that the chlorine monoxide dissolves but little of the chlorine is absorbed. The unused chlorine is then recycled.[8] Hydrochloric acid may also be removed by the use of insoluble metal oxides or carbonates, or soluble alkalis. Thus chlorine and water may be passed into an absorption tower packed with calcium carbonate,[9-11] or calcium oxide.[12] Hypochlorous acid is so weak that conditions can be selected under which hydrochloric acid, but not hypochlorous acid, is neutralized. Sodium bicarbonate can be used for this purpose.[9] Continuous processes have also been developed which involve passing a solution of alkali or alkaline earth hydroxide or hypochlorite down a scrubbing tower, with counter-current flow of chlorine.[13-15] The hypochlorous acid produced by these processes is either filtered,[10,12,14] distilled,[15] or extracted with some suitable solvent,[9] such as carbon tetrachloride, chloroform, dichloroethane, tetrachloroethane and diethyl ether. These solvents extract the hypochlorous acid from aqueous solution, but not the chloride which is also formed in quantity. Extraction is improved by the addition of small quantities of short chain primary (methyl–butyl) alcohols. If the alcohols are added alone to hypochlorous acid solutions, an insoluble compound (presumably the alkyl hypochlorite) separates, and is removed by decantation, solvent extraction, or evaporation in a current of air. The ester may then be hydrolyzed by strong alkali.[9]

A stable solid which will yield hypochlorous acid on treatment with water may be prepared by mixing magnesium hypochlorite with sodium hydrogen sulphate. This solution will, of course, be heavily contaminated with other ions.[16] This contamination is less if calcium phosphate is mixed with calcium hypochlorite, treated with water, and the solution acidified with sulphuric acid to pH 4·5 – 7.[17]

The Properties of Hypochlorous Acid and of the Hypochlorites in General.

Hypochlorous acid is not sufficiently stable to exist as the pure acid and is commonly used in aqueous solution. From the freezing points of the aqueous solution,[1] and the fact that the distribution of hypochlorous acid between solution and vapour is independent of concentration,[18] it is evident that hypochlorous acid is not associated in aqueous solution. A comparison of the absorption spectrum of the aqueous solution with that of the vapour does suggest however that there may be considerable interaction with the water dipoles.[19] The absorption spectra for solution and vapour are shown in Fig. 1. The hypochlorous acid for these measurements was prepared by distilling a mixture of bleaching powder, boric acid and water under reduced pressure. Traces of chloride were removed by redistillation over silver sulphate. To obtain the absorption spectrum for the vapour, light was transmitted through a tube 10 metres long, heated electrically to about 45°C. A hypochlorous acid solution was heated, and the vapour passed along the tube.

There is a considerable difference between the extinction coefficients, ε, obtained in the vapour and dissolved states. Since solutions of hypochlorous acid can be so readily distilled, it is probable that the acid exists as the molecular form HOCl in the vapour phase. An alternative concept, that the acid dissociates entirely into chlorine monoxide and water in the vapour, may be dismissed on the grounds that: (*a*) the vapour spectrum (Fig. 1) does not resemble that of chlorine monoxide (see page 516), and (*b*) although the extinction coefficients differ, the general form of the vapour and solution curves is similar. The difference cannot be ascribed to chlorine dioxide, which has a readily detected band spectrum. The spectra show two main absorption regions; these may result from dissociation into OH + Cl, HCl + O, or H + ClO, but a particular dissociation process has not been assigned to either band with certainty.[19] It is feasible to attribute the difference between the two curves to dipole association in aqueous solution, but this is not entirely satisfactory, since an aqueous solution of hypochlorous acid has been shown to give the same absorption spectrum as a solution of ethyl hypochlorite in petroleum ether.[20] It is more likely therefore that the difference results from abnormality in the gaseous, rather than in the dissolved, molecule.

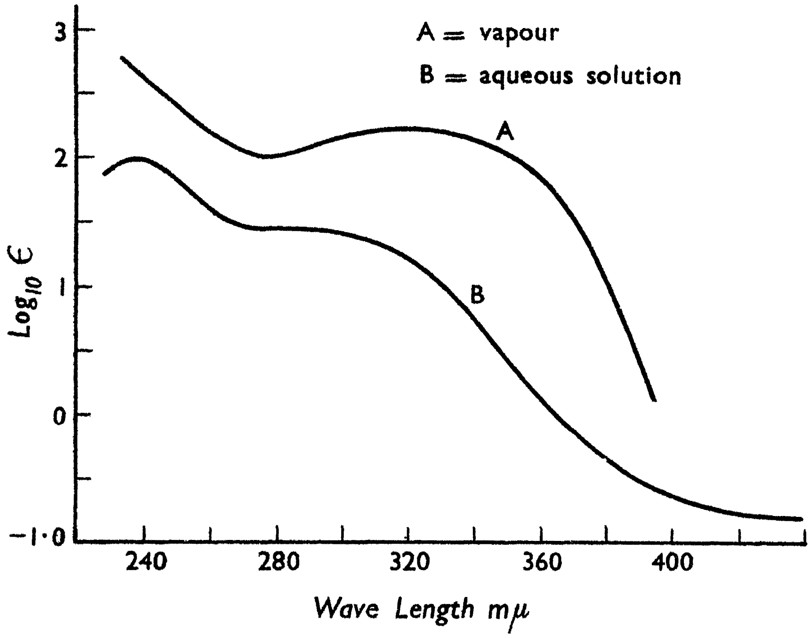


Fig. 1. ABSORPTION SPECTRUM OF HYPOCHLOROUS ACID

The heat of formation of HOCl(aq) from the elements has been determined as[21] 29·29 and[22] 29·22 kg.-cal./mol. The heat of formation of HOCl(aq) from chlorine and the alkali metal hydroxides is 30·44 (± 0·1%) kg.-cal./mol.[23] The heat of neutralization of hypochlorous acid with strong alkalis is 8·94 kg.-cal./mol.; the values obtained with lithium, sodium, potassium, calcium, strontium and barium hydroxides are almost the same, which is held to indicate that hypochlorous acid is only slightly dissociated in aqueous solution. Heats of dilution of aqueous solutions over a range of concentration have also been determined by a calorimetric method.[23]

Hypochlorous acid is a weak acid. This, combined with its instability, has made the accurate determination of its dissociation constant difficult. The scatter in the experimental values is shown in Table XV.

TABLE XV.- DISSOCIATION CONSTANTS OF HYPOCHLOROUS ACID

Dissociation Constant K ($\times 10^8$)	Temp. °C.	Reference
1·0	25	18
0·067	25	24,25
2·8	5	26
3·01,2·95	25	27
3·2	15	28
3·47	18	29
3·6	25	30
3·7	20	31
5·6	25	32
6·4	25	33
10·5	25	34
14·6	25	35
1·04	20	36
1·18	30	36
6·8	25	37

The more recent values are in reasonable agreement, and the true value is probably between 3×10^{-8} and 4×10^{-8}; ionic dissociation is therefore extremely small.

Hypochlorous acid decomposes on standing. There are two modes of decomposition:-

$$2HOCl \rightarrow 2HCl + O_2$$
$$3HOCl \rightarrow 2HCl + HClO_3.$$

Since the free ions undergo similar decomposition, the salts are also unstable, though their decomposition is usually slower. The mode, and the rate, of decomposition can be influenced considerably by temperature, concentration, pH, added salts, exposure to atmosphere and illumination. Since the first reaction is responsible for the oxidizing and bleaching action of hypochlorites, the decomposition has been studied under a variety of conditions. Sodium hypochlorite solutions with 10% available chlorine lose about 0·017% daily; the concentration falls to half strength in about a year, and from 10·74 to 3·40% in two years.[38] Early attempts to explain the mechanism of decomposition were based on a series of collateral reactions which included the intermediate formation of chlorite.[39] However, added chloride ions influence the velocity of decomposition, and it is not necessary to assume such collateral reactions.[40,42] At constant pH, the reaction is autocatalytic, the velocity being proportional to the chloride ion concentration and to the square of the hypochlorite ion concentration. The catalytic effect of the nitrate ion is much less than that of the chloride ion,[41] and sodium hypochlorite made from very pure reagents is much more stable than that containing traces of catalytic impurity. Catalysts generally increase the rate of both modes of decomposition, but the increase is less pronounced in the reaction forming chlorate.[43]

The rate of decomposition of sodium hypochlorite solutions free from traces of heavy metals has been studied at 45° in the presence of various added salts, including sodium chloride, sodium sulphate, sodium dihydrogen phosphate and calcium chloride.[44] The experiments were confined to the initial stages of the decomposition, where the reaction:-

$$2ClO^- \rightarrow 2Cl^- + O_2$$

is not complicated by the chlorate ions which appear as reaction proceeds. The Brönsted theory may be applied to the reaction; the decomposition rates have been substituted in the equation:-

$$h = kC_AC_B\ 10^{Z_AZ_B\sqrt{\mu}}$$

(h = reaction velocity, k = velocity constant, C_A and C_B are the molar concentrations and Z_A and Z_B the valencies of ions A and B, and μ the ionic strength of the solution). A positive salt effect is to be expected in this reaction; the slope of the plot of log k against $\sqrt{\mu}$ is found to be +1, in full agreement with the above mode of decomposition. The velocity data show the reaction to be kinetically bimolecular in strong salt solutions.[44] Other experiments, also at 45°, indicate that decomposition is bimolecular only so long as the solution remains alkaline;[45,46] in acid solution the order of reaction could not be determined definitely.[45]

The pH of the solution influences not only the rate but also the mode of decomposition. Dilute hypochlorite solutions are most stable at pH 13·1, and least stable at pH 6·7.[47] Maximum chlorate formation has been observed in weakly alkaline medium,[45] and at pH 7·13.[48] Oxygen evolution is less as chlorate formation increases; for potassium and sodium hypochlorites, at 20°, the evolution of oxygen goes through a minimum at pH 7, and is maximal at an acid concentration corresponding to a solution of 0·5 g. of orthoboric acid in 10 ml. of water. Lithium hypochlorite behaves differently, and the oxygen evolution increases slowly with pH. Under the same conditions, the rate of decomposition of the salts KOCl, NaOCl and LiOCl decreases in the order named. The formation of alkali peroxides was believed to be a rate-determining reaction, although the addition of alkali peroxides or hydrogen peroxide gave negative results.[49] The influence of pH on decomposition rates appears, from limited data, to be less at higher temperatures than at room temperature. The velocity constant K for sodium hypochlorite decomposition has been determined at 31° and at 46°, and in 0·30 and 0·381 N-sodium hydroxide solution. In 0·30 N-alkali, $K_{31°} = 0{\cdot}0006$ and $K_{46°} = 0{\cdot}0042$. In 0·381 N-alkali, $K_{31°} = 0{\cdot}00035$ and $K_{46°} = 0{\cdot}0042$. At the higher temperatures the velocity constant appears to be independent of alkali concentration, but the concentration difference is not sufficient to establish this.[50]

Illumination greatly accelerates the decomposition of hypochlorous acid[51] and of metal hypochlorite solutions.[52,53] The products of photodecomposition are the same as for the dark reactions, hydrochloric and chloric acids and oxygen being produced. At temperatures above 50°, visible rays were found to be more active than ultra-violet, which had little effect; hypochlorous acid was also found to be less sensitive to light than its sodium salt.[54] At room temperature the reverse is the case.[55] For photodecomposition of hypochlorous acid, the quantum efficiency is between 2 and 3. The proposed mechanism is represented by the steps:-[51]

$$\begin{aligned} &(a)\ HOCl + h\nu \rightarrow HCl + O \\ &(b)\ O + HOCl \rightarrow HCl + O_2^* \\ &(c)\ HOCl + O_2^* \rightarrow HClO_3 \\ &(d)\ O_2^* \rightarrow O_2 \end{aligned}$$

Reactions (c) and (d) are concurrent and competing reactions. For reactions (a), (b) and (c), the quantum efficiency is 3, and the overall reaction is $3HOCl \rightarrow 2HCl + HClO_3$. For reactions ($a$), ($b$) and ($d$), the quantum efficiency is 2, and the overall reaction $2HOCl \rightarrow 2HCl + O_2$. The yields of chloric acid (and thus the quantum efficiency) are considerably increased by adding sodium phosphate, and to a smaller extent by adding lithium sulphate and sodium sulphate. Yields are slightly decreased by adding sulphuric acid, but more so by adding ionic chlorides, which are effective in the order HCl>KCl>LiCl.[51] The photodecomposition of sodium hypochlorite solutions resembles that for hypochlorous acid. Using a wave-length of 3650 A., the quantum efficiency decreases with decreasing concentration. Decrease in wave-length, or addition of sodium chloride, increases the quantum efficiency, and thus the yield of chlorate compared with that of oxygen. At a wave-length of 2540 A. this increase in quantum efficiency is pronounced. The above mechanism is then inadequate to explain the results, and it is suggested that in this case the absorbed quantum activates an O_2 molecule to a sufficient extent to enable it to split off atomic oxygen from the ClO^- ion.[55]

Because the decomposition of the hypochlorite ion is an important factor in bleaching operations, much work has been done on the behaviour of various materials as catalysts or 'activators' for this decomposition.[65] The addition of metals, their oxides or hydroxides, has a pronounced effect on the decomposition rate. The efficiency of the metals themselves varies widely; aluminium, lead, zinc and iron are not so effective as manganese, cobalt and nickel.[56] If the decomposition rate is expressed in the form:-

$$d[OCl]/dt = -k[OCl^-]^2$$

then the catalytic action of various metal hydroxides may be compared from the following values of k, which were obtained when small quantities of the hydroxide were added to 0·05 molar sodium hypochlorite at 25°:-

Hydroxide of:	Co	Ni	Cu	Sn	Fe
$k =$	75	51	44	2·5	0·5

In the absence of a catalyst, k was 0·01.[57] In these catalyzed decompositions the velocity is again retarded by increase in pH, and is accelerated by increase in temperature. With increasing hypochlorite concentration, however, the decomposition rate at first decreases, then becomes constant.[56] The decomposition rate of sodium hypochlorite solutions has been studied also in the presence of copper snd iron compounds,[61] cobalt and nickel oxides,[58] and cobalt, copper and iron oxides.[59] The presence of free alkali reduces the reaction velocity with both nickel and cobalt oxides. These oxides are added as the higher oxides NiO_2 and CoO_2; although they are termed 'peroxides' there is some doubt as to their true constitution. This uncertainty however is less important than might appear, since the normal oxides are converted by hypochlorite into the higher oxides, and the oxide responsible for catalysis may not therefore be the one added initially. Using the oxide CoO_2, the specific reaction constant is proportional to the quantity of catalyst added.[60] Reaction velocities in this experiment (as in most others) were determined from the rate of oxygen evolution. The effectiveness of the catalyst was found to decrease with repeated use. Addition of sodium chloride increases the value of the reaction constant, the increase being proportional to the square root of the sodium ion concentration. An increase in sodium ion concentration probably results in higher adsorption of the hypochlorite ion on the catalyst surface. The catalyst will no doubt influence the decomposition rate by forming intermediate compounds at its surface; the nature of these compounds may depend, in turn, on the structure of the catalyst oxide. An attempt has been made to devise a reaction scheme,[60] but this scheme assumes that the oxide CoO_2 is a peroxide, which is unlikely. The temperature coefficient of reaction, for decomposition catalyzed by cobalt dioxide, is 2·37 for a 10° rise in temperature.[60]

The catalytic effect of metals and their compounds may be enhanced by the addition of 'promoters'. Thus, alumina gel is without appreciable effect on sodium hypochlorite, but together with cobaltic oxide it shows a promoter action which is a maximum at about 26 - 39% of alumina. With nickel oxide, alumina gel shows at first a marked promoter action, but larger quantities have a 'depressor' action; this may be due to occlusion of the nickel oxide within the gel, where it would be no longer available for hypochlorite adsorption.[58] Mixtures of the higher oxides of cobalt and nickel are more efficient catalysts, weight for weight, than either oxide singly, and the effect is at a maximum at about 30% nickel oxide. Oxide gels have been arranged in the following order of decreasing catalytic activity: Ni>Co>Cu>Fe>Mn>Hg. The catalytic activity of copper oxide is enhanced by the addition of magnesium oxide,[59] (although the latter does not catalyze hypochlorite decomposition), and ferric oxide.[62] The maximum promoter effect is obtained when the oxides are present in the ratio Cu : Mg = 1 : 4, and Cu : Fe = 1 : 1.[59,62] It is suggested that the promoter functions by preventing agglomeration of the particles of catalyst and thus preventing the destruction of active centres.[62]

Ammonia and related compounds also accelerate the decomposition of hypochlorites, although in this case direct chemical reaction is involved. Reaction with ammonium hydroxide is firstly:-

$$NaOCl + NH_4OH \rightarrow NaOH + NH_4OCl.$$

Ammonium hypochlorite is unstable, the overall reaction for its decomposition being:-

$$NH_4OCl \rightarrow NH_4Cl + O,$$

but the reaction proceeds via the formation of monochloroamine:-

$$NH_4OCl \rightarrow H_2O + NH_2Cl,$$

which can react further with hypochlorite:-

$$NH_2Cl + NaOCl \rightarrow NHCl_2 + NaOH.$$

Hydrolysis of the chloroamines gives ammonium chloride and oxygen. On adding ammonium hydroxide to sodium hypochlorite solution, decomposition is greatest when the $NaOCl : NH_4OH$ ratio is 2 : 1, and is a minimum when it is 1 : 1. The temperature coefficient of reaction is 1·94.[63,64] These reactions are very rapid when ammonium salts are used. With ammonium carbonate, oxalate, nitrate, acetate and phosphate, decomposition of hypochlorite takes place within a few seconds. By the use of alkyl-substituted compounds, the decomposition rate can be reduced. Thus in the series urea, ethylurea, diethylurea, ethyl and diethylammonium chloride and methylammonium chloride, the time required for decomposition of 80% of the hypochlorite varies from 20 - 30 minutes to 5 - 6 hours.[64] In all cases chloroamine-type compounds are formed.

Solid hypochlorites also undergo decomposition. Experiments on storage of calcium hypochlorite showed that at 25° the internal pressure of sealed containers may be increased by 10% owing to oxygen evolution; at 100 - 112° calcium hypochlorite decomposed rapidly, and often violently.[66] The stability of solid sodium hypochlorite varies with the degree of hydration. Thermal data and solubility curves indicate the existence of the three hydrates $NaOCl, 5H_2O$ (m.p. 24·5°), $NaOCl, 2{\cdot}5H_2O$ (m.p. 57·5°), and $NaOCl, H_2O$. At room temperatures the pentahydrate liquefies in the course of a few hours, and decomposition occurs by both routes, to give chloride with chlorate, and chloride with oxygen. The decomposition is greatly accelerated by carbon dioxide in the air.[67] The stability of solid sodium hypochlorite increases as the degree of hydration is decreased, and the technical product (which corresponds approximately to $NaOCl, 4H_2O$) may be stabilized by passing carbon dioxide-free air over the crystals, maintaining the temperature below the melting point of the crystals, until the degree of hydration is reduced to 2 – 3 molecules of water per hypochlorite molecule.[68]

Various methods have been suggested for stabilizing hypochlorites for commercial use. They should be stored in the dark,[69] kept out of contact with air and freed from dissolved oxygen as far as possible,[70] and in tropical climates decomposition is reduced by storage in a refrigerator.[71] Stabilizing agents for hypochlorite solutions include sodium silicate,[69,77] alkalies[78,79] and potassium permanganate.[69] The addition of sodium bicarbonate to sodium hypochlorite in the molecular ratio 2 : 1 stabilizes the solution.[80] Agents suggested for stabilizing solid hypochlorites include sodium chloride free from magnesium chloride and other hygroscopic impurities,[72,73] sodium sulphate,[74] sodium monoxide[75] and sodium carbonate.[76]

The oxidizing power of hypochlorous acid and the hypochlorites is modified by the presence of activators. These additives have been referred to in connection with the decomposition rates of hypochlorites, since any compound which accelerates the decomposition rate also enhances the oxidizing properties of hypochlorites. Hydrogen peroxide can serve as an activator of a different type, and the kinetics of the hypochlorous acid-hydrogen peroxide system have been studied. Reaction is most rapid at pH near 8, where the hypochlorous acid is least stable,[81] and takes place between the hypochlorite ion and hydrogen peroxide molecule:-

$$ClO^- + H_2O_2 \rightarrow H_2O + O_2 + Cl^-.$$

This is the rate-determining step; reaction is of second order, and the rate constant is $1{\cdot}7 \times 10^5$ litres/mol.min. at 25° The reaction has an activation energy of 11·6 kg.-cal./mol.[82] In connexion with the mechanism of hypochlorite oxidation, the oxidation potentials of some hypochlorite solutions have been measured,[83,84] and the anodic oxidation process studied.[85]

Hypochlorites oxidize bromides to hypobromites and bromates, and iodides to hypoiodites and iodates. These reactions depend to a considerable extent on pH and temperature. Within the pH range 10 – 13, reaction with a bromide produced only hypobromite; the reaction is of second order, and the rate-determining step is probably:-

$$HOCl + Br^- \rightarrow HOBr + Cl^-.$$

Under these conditions no other oxyacid ions are formed. At 25°, the rate constant is $1{\cdot}77 \times 10^5$ litres/mol.min., and the dependence of reaction on temperature gives an activation energy of 15 kg.-cal./mol. for this reaction.[86] A similar reaction with iodides forms the basis of a method for the quantitative determination of the hypochlorites. If the latter are titrated with iodide in sodium bicarbonate solution, the hypoiodite first formed is unstable, and is converted to iodate, so that the reaction is:-

$$3HOCl + I^- \rightarrow IO_3^- + 3H^+ + 3Cl^-$$

At the end point, addition of excess iodide gives free iodine.[87]

Sodium thiosulphate is oxidized to sodium sulphate by hypochlorites. If the hypochlorite is added to excess of thiosulphate, reaction is not quantitative since some sulphur escapes oxidation by forming hydrogen sulphide. Reaction is quantitative, however, if the reagents are mixed in the reverse order; it may be followed by potentiometric titration, when the end-point is indicated by a change in potential of the order of 800 mV.[88] Sodium thiosulphate is oxidized less readily by hypochlorous acid than by hypoiodous acid.[89] Solutions of metal sulphides react with an excess of a hypochlorite to form sulphur and sulphate, in quantities which depend on the relative concentration of reactants, temperature and pH. The initial reaction involves formation of sulphur:-

$$Na_2S + NaOCl + H_2O \rightarrow NaCl + 2NaOH + S;$$

the sulphur is then oxidized, by stepwise addition, to the sulphate ion. As expected, the highest $SO_4 : S$ ratio is obtained in high hypochlorite concentrations.[90]

Under favourable conditions ammonia may be oxidized to nitrogen by hypochlorites, but the reaction is always far from quantitative since it is difficult to prevent the formation of chloroamines referred to above.[91] In volumetric determinations, ammonia oxidation may be carried out by neutralizing the solution, adding potassium bromide, and titrating it with calcium hypochlorite solution. In this procedure the oxidizing agent is the hypobromite ion, which is a stronger oxidizing agent than the hypochlorite ion. Even so, results are satisfactory only with less than 10 mg. of ammonia, and are erratic with larger quantities of ammonia.[92 93] The bromide–hypochlorite mixture, in the presence of sodium bicarbonate, has been used successfully to determine thiocyanates, thiosulphates, cyanides,[94] hydrazine, selenites and tellurites,[92] though the two latter are oxidized quantitatively by calcium hypochlorite alone. Some of the difficulties involved in the use of hypochlorites may be overcome by the use of chloramine-T, which is hydrolyzed to give sodium hypochlorite in dilute acid solution:-[95,96]

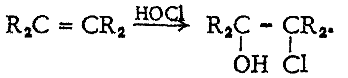
$$CH_3.C_6H_4.SO_2N.NaCl + H_2O \rightarrow CH_3.C_6H_4.SO_2NH_2 + NaOCl.$$

Its aqueous solution is much more stable than is a hypochlorite solution, and it has been used with success for the determination of arsenic, antimony and tin salts, thiosulphate, sulphite and sulphide, cyanide, thiocyanate and ferrocyanide. In the presence of potassium bromide the oxidizing powers are increased; hydrazine is oxidized to nitrogen, but direct titration of ammonium salts is again unsatisfactory.[96] The reaction between hypochlorite and nitrites is highly dependent on pH; for pH values over 10, oxidation of nitrite does not occur,[97] although oxidation occurs quantitatively on titrating a solution of sodium nitrite with a chloramine-T solution in the presence of potassium iodide.

Manganese salts are oxidized by hypochlorites to permanganates. The red colour sometimes observed in calcium hypochlorite is attributed to oxidation of traces of manganese salts.[98] The readiness with which this oxidation occurs can be influenced considerably by added salts, and the effect of added copper and cobalt salts has been investigated in detail.[99] Added to a solution of nickel sulphate, sodium hypochlorite produces a black hydrated nickel dioxide, the properties of which vary with temperature and conditions of precipitation.[100]

Bleaching.

There are three main reactions which account for the bleaching action of hypochlorous acid and hypochlorites on organic colouring matters; the latter may be chlorinated (which happens with saturated compounds) or oxidized (when extensive breakdown of the molecule frequently occurs) or with unsaturated compounds the hypochlorous acid may add to a double bond in the form OH + Cl:-



$$R_2C = CR_2 \xrightarrow{HOCl} \underset{OH}{R_2C} - \underset{Cl}{CR_2}.$$

Bleaching with hypochlorous acid is not usually a reversible process. No single molecular or ionic species is responsible for bleaching, and the best conditions depend largely on the composition of the compound to be bleached. Dyestuffs are normally unsaturated; the rate of bleaching of several dyes by hypochlorous acid has been found to increase on adding sodium chloride, sodium hydroxide or hydrochloric acid, particularly the latter. The variation in electrical conductivity during the bleaching of Orange II by hypochlorous acid in the presence of hydrochloric acid showed no appreciable increase in the concentration of the latter. No oxidation takes place therefore, and bleaching is due to addition of HOCl across a double bond.[101,102] Bleaching efficiency in such a case will depend on hypochlorous acid concentration; it may be increased by a factor of 5 by addition of sodium bicarbonate,[103] and this is attributed to the reaction:-

$$\mathrm{NaOCl} + \mathrm{NaHCO_3} \rightarrow \mathrm{Na_2CO_3} + \mathrm{HOCl}.$$

Sodium bicarbonate will also neutralize the sodium hydroxide formed in the hydrolysis:-

$$\mathrm{NaOCl} + \mathrm{H_2O} \rightarrow \mathrm{HOCl} + \mathrm{NaOH},$$

and thus minimize the reverse reaction. A similar explanation may account for the catalytic effect of hydrochloric acid, although if a calcium hypochlorite solution is brought to the same pH value (7·6) by sodium bicarbonate or hydrochloric acid, the bicarbonate solution is the more efficient bleach.[104] These solutions are valuable for immediate use, but if the solution is to be stored, a high concentration of hypochlorous acid leads to decomposition into chlorate:-

$$\mathrm{ClO^-} + 2\mathrm{HOCl} \rightarrow \mathrm{ClO_3^-} + 2\mathrm{H^+} + 2\mathrm{Cl^-}.$$

Since the rate of chlorate formation is proportional to $[\mathrm{HOCl}]^2$, it can be greatly reduced by the addition of a small excess of alkali. Reference should also be made to several other papers in which the optimum conditions for using hypochlorite solutions for bleaching fabrics and wood pulp are discussed,[105-109] and to the kinetics of hypochlorite bleaching.[110]

The action of hypochlorites on the material to be bleached is another factor in their use as bleaching agents. Cellulose is oxidized slowly, and the presence of metals or their salts (such as copper, iron, copper soaps, iron rust) catalyzes this oxidation.[111] Hypochlorous acid causes slight dissolution of wool as a whole; chloroamines are not detected when wool is treated with hypochlorous acid, though they are formed when chlorine acts on wool. Hypochlorous acid reacts with the carboxyl groups in wool protein, since wool so treated will no longer condense with semicarbazide.[112] Treatment of wool with calcium hypochlorite results in scale and cortical-tissue chlorination.[113]

Corrosion.

Many metals and alloys are corroded by hypochlorite solutions, and it is unfortunate that alkalies and salts added to stabilize the hypochlorite frequently increase the corrosive properties of the solution. Using commercial sodium hypochlorite solutions, some metals tested have been arranged in the following order of increasing corrodibility: monel metal, steel, nickel, tin, copper.[114] A solution of sodium hypochlorite (255 p.p.m.) was found to dissolve tin at the rate of 0·12 mg./sq.cm./hour.[115] In the case of nickel, tin, stainless steel and monel metal, both sodium phosphate and detergents reduced the rate of corrosion.[115] Sodium silicate is also a good corrosion inhibitor.[117] Some reports on corrodibility are apparently conflicting; thus aluminium is said to be readily attacked by hypochlorite solutions,[116,117] and to be resistant.[118] Iron containing chromium is reported as resistant,[118,119] but also to be corroded.[117] This may be due partly to the use of different metal samples, but it arises mainly from the differing standards used to define negligible corrosion; what may appear as negligible corrosion on a large-scale trial may be readily measurable under laboratory conditions. Hypochlorite solutions may be used to blacken copper:[120] a fine, evenly distributed coating of copper oxide is produced by immersing clean copper in a sodium hypochlorite solution containing sodium hydroxide and an alkali metal phosphate.

Uses.

Apart from their very general use as bleaching and disinfecting agents, hypochlorous acid and the hypochlorites have been used for a number of more specialized purposes, for example in water sterilization, textile finishing,[121] anti-algæ treatment of refrigerator water,[124] air purification,[125,126] and as deodorizers and bactericides.[122,123] Sodium hypochlorite, together with a sulphonate wetting agent, is used as an insecticide,[127] and hypochlorites have been suggested for the selective oxidation of minerals.[128] Organic sulphur compounds in coal gas and petroleum may be removed by treatment with sodium hypochlorite.[129-131] Although the latter has little action on thiophen, hypochlorous acid attacks thiophen readily, about 15% of the thiophen sulphur being oxidized to sulphate, and thiophen may be removed from benzene by this means. Acidification of a sodium hypochlorite solution with acetic acid to pH 4 gives an effective reagent, and using thiophen, hypochlorite ion and acetic acid in the ratio 1 : 5 : 16, thiophen removal was found to be complete.[132] Carbon black is rendered hydrophilic by treatment with sodium hypochlorite; a stable suspension in water can therefore be formed, and in the formation of hardened rubber this suspension can be mixed with the latex without coagulating the latter.[133] Hypochlorous acid also finds extensive use in preparative chemistry by virtue of its ability to add to carbon–carbon double bonds. The hypochlorous acid is not usually prepared separately, and it is often sufficient to pass chlorine and the unsaturated compound into water at the same time. The chlorine is hydrolyzed, and the hypochlorous acid so formed reacts immediately. Using ethylene, ethylene chlorohydrin is formed,[134] and its hydrolysis provides ethylene glycol.

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THE HYPOCHLORITES

The preceding sub-section being concerned with those general properties of hypochlorites which may be regarded as characteristic of the hypochlorite ion, the present sub-section deals with the preparation and properties of particular salts. Some aspects of preparative work that are common to a number of preparations are mentioned first. The important reaction is still that between chlorine and an alkaline solution:-

$$Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O;$$

the reaction is usually stopped before completion, since the free alkali remaining enhances the stability of the solution.[1-5,18-20] Solid mixtures of hypochlorite and chloride are obtained by suspending the anhydrous alkali hydroxide in carbon tetrachloride, and treating the suspension with chlorine. Since alkali hypochlorites are insoluble in carbon tetrachloride, the product may be filtered off and dried.[6] The chlorine may be replaced by a mixture of chlorine with chlorine monoxide, or by chlorine monoxide alone.[7] Hypochlorites are usually prepared as mixtures with chlorides, but can readily be separated from chloride. For example, addition of acetanilide or other amine base to an aqueous solution gives the chloryl derivative of the base, while the chloride has no action. The chloryl compound may be separated, and treated with an alkali hydroxide (such as calcium hydroxide), to form the corresponding hypochlorite.[9] In place of acetanilide, *tert.*-amyl alcohol or other tertiary alcohol may be used; the tertiary alkyl hypochlorite is separated from solution, and is treated with alkali hydroxide.[10,11] This reaction can also be carried out between the solid alkali and the alkyl hypochlorites in the vapour phase with a small proportion of water; for example, calcium hypochlorite is prepared by treating lime with the vapour of *tert.*-butyl hypochlorite.[12] The addition of a small quantity of an arylsulphonamide stabilizes solutions of metal hypochlorites. The sulphonamide takes up any hypochlorous acid formed by hydrolysis, and this inhibits the $HOCl-ClO^-$ decomposition reaction.[17] For some purposes it is convenient to use hypochlorites in conjunction with soaps. In these cases a convenient solid solution is obtained by making an aqueous alkaline solution of the sodium salt of caprylic, caproic, capric or lauric acid of such concentration that the soap will separate on cooling the hot solution. The solution is saturated with chlorine when hot, and then allowed to solidify by cooling.[13-16]

Lithium hypochlorite is prepared by chlorination of lithium hydroxide solution. Using a saturated solution of the hydroxide, a solution containing about 10% of lithium hypochlorite is obtained. If the solution is evaporated until it contains about 25% lithium hypochlorite, a crystal crop containing about 50% lithium hypochlorite may be obtained. On drying the crystals, 26% of water remains, corresponding to the monohydrate, $LiOCl,H_2O$.[22] Anhydrous lithium hypochlorite may be prepared by removing water from the monohydrate at temperatures in the range 20 - 60°, under a pressure of less than 0·1% of the vapour pressure at the temperature used.[24-26]

Treatment of an alkaline earth hypochlorite with lithium carbonate or sulphate gives lithium hypochlorite which is virtually chloride-free.[24] If a solution of the hydroxides of lithium, sodium and potassium is chlorinated, the quantity of lithium chloride produced, (relative to the hypochlorite), is reduced by the presence of sodium and potassium hydroxides. From the resulting solution, sodium and potassium chlorides can be removed by evaporation and crystallization.[21,24] Lithium hypochlorite is a useful bleaching agent, and has high stability;[23] it was found to lose 2% of its available chlorine in 53 days, under conditions in which sodium hypochlorite lost 30% of available chlorine in 40 days.[22] The use of *tert.*-butyl alcohol in the purification of lithium hypochlorite monohydrate has been described.[27]

Sodium hypochlorite is formed when a concentrated aqueous solution of sodium hydroxide is shaken with a solution of chlorine monoxide in carbon tetrachloride. The crystalline product, (approximating to $NaOCl,2{\cdot}5H_2O$), is rather unstable and loses oxygen on standing, though the decomposition of anhydrous sodium hypochlorite is not detectable for several weeks.[28] Potassium hypochlorite is prepared similarly; it is less stable than the sodium compound, and decomposes to give the orange oxide, K_2O_3:-

$$2KOCl + Cl_2O \rightarrow K_2O_3 + 2Cl_2.$$

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Solid mixtures of sodium (or potassium) chloride and hypochlorite are obtained when a fine spray of the alkali hydroxide is treated with chlorine gas.[31] A stabilized preparation of sodium hypochlorite in solid form is formed by adding to the molten compound an anhydrous salt which is itself capable of forming a stable hydrate, such as sodium metaborate or trisodium phosphate.[39,40] To maintain the necessary alkalinity in the preparation of sodium hypochlorite solutions by the reaction of chlorine with sodium hydroxide, the use of a buffered solution is desirable. Sodium carbonate, phosphate, tetraborate and silicate are suitable buffering agents, and the end point of the reaction can be determined by the use of suitable indicators.[29] The colour change in p-nitrophenol from yellow-green to yellow is found to correspond with the best yield of sodium hypochlorite.[30] Sodium hypochlorite solutions free from caustic soda may be prepared by the chlorination of sodium carbonate solutions. In one method, the chlorine is bubbled through a suspension of sodium carbonate in its saturated solution until almost all the carbonate is converted to bicarbonate.[32,33] It is important that this stage should not be passed, since very unstable solutions result from the chlorination of sodium bicarbonate solutions. The reaction then is:-

$$NaHCO_3 + Cl_2 \rightarrow NaCl + CO_2 + HOCl,$$

and proceeds without the formation of sodium hypochlorite.[37]

A solution of sodium hypochlorite suitable for medicinal purposes is prepared by adding calcium hypochlorite to a hot aqueous solution of sodium carbonate and filtering the solution.[34] It is also claimed that conditions suitable for the preparation of stable, concentrated sodium hypochlorite solutions are obtained if sodium hydroxide is treated with chlorine in the presence of salts of metals which give amphoteric hydroxides, such as aluminium chloride. Aluminium hydroxide separates from the solution; it helps to prevent overchlorination, and is readily removed by filtration.[6] The use of sodium aluminate or sodium zincate as a stabilizing agent has therefore been suggested also.[38] The stabilization of hypochlorite solutions has already been discussed (see page 551); for sodium hypochlorite the necessity of maintaining an alkaline solution was one of the earliest observations.[35] Small quantities of metal salts likely to catalyze decomposition may be precipitated by giving the hypochlorite a preliminary treatment with alcohol or acetone.[36] The influence of sodium hydroxide on the stability of sodium hypochlorite solutions (prepared by chlorination of sodium carbonate) is illustrated by an experiment in which a solution containing 100 g./litre of sodium carbonate was treated with chlorine. Stable solutions having chlorine contents up to 20 g. of chlorine per litre were obtained. With this extent of chlorination the free alkalinity was equivalent to not less than 4 g. per litre of sodium hydroxide. When the chlorine content was increased to 22 g. per litre the alkalinity fell to 0·18 g. sodium hydroxide per litre, and the solution then lost 50% of its chlorine within 24 hours.[37]

The existence of ammonium hypochlorite is doubtful; formation of monochloroamine by the reaction of ammonium salts with hypochlorites has been referred to (see page 550). When ammonia is added to a solution of sodium hypochlorite, the characteristic hypochlorite reaction with aniline fails when the $NH_3 : NaOCl$ ratio reaches 1 : 1.[41]

Magnesium hypochlorite is prepared from calcium hypochlorite and magnesium chloride. Concentrated aqueous solutions of the two salts are mixedm and allowed to stand for ten hours. The precipitated magnesium hypochlorite is filtered off and dried rapidly in a vacuum.[47,48] The action of chlorine on an aqueous suspension of magnesium oxide or hydroxide produces a basic hypochlorite which is fairly stable in the solid state.[42-46]

Chlorination of a suspension of calcium hydroxide in water at 15-45°

produces the following compounds: $Ca(OCl)_2,2Ca(OH)_2$; $3Ca(OCl)_2,2Ca(OH)_2,2H_2O$; and $Ca(OCl)_2,3H_2O$.[49,50] A practical difficulty in the preparation of calcium hypochlorite results from the fact that under these conditions it is usually precipitated in microcrystalline form. The hypochlorite may be formed at the expense of the basic hypochlorites, as follows. A suspension of calcium hydroxide is chlorinated at a rate per minute equal to 1 - 2% of the quantity of chlorine required for complete chlorination, and at a temperature of 15°. The calcium chloride content of the solution is kept constant, (30 - 35%), by continuous addition of calcium hydroxide. The mixture is then seeded with crystals of the pure compound, $Ca(OCl)_2,3H_2O$, and an easily filterable product of this composition is obtained.[49,51] If basic calcium hypochlorites are produced in this process, they may be converted to the neutral hypochlorite by filtration from the mother liquor (or precipitated from the mother liquor by the addition of more lime); the basic salts are then suspended in water and submitted to further chlorination.[52-54] These conditions produce neutral calcium hypochlorite in the form of easily filterable, tetragonal plates.[55] The chlorination process can also be carried out using lime and liquid chlorine.[56] Calcium hypochlorite crystals may be dried and dehydrated in a current of dry air at a temperature of 140 - 150°.[64-66] The two basic hypochlorites $Ca(OCl)_2,Ca(OH)_2$ and $Ca(OCl)_2,2Ca(OH)_2$ are prepared by heating a clear solution of bleaching powder with added calcium hydroxide. The solution is evaporated at 40° until the basic hypochlorites separate. The monobasic salt is obtained when the solution contains not less than 10% of available chlorine, and the dibasic salt when the available chlorine falls to 6·5%. The crystals may be dried at 115° at atmospheric pressure, or at 80° in a vacuum.[57] Dibasic calcium hypochlorite is not readily filtered, but the particle size may be increased by adding, to a suspension of the compound in water, calcium hydroxide and hypochlorite ions in approximately the proportions required by the dibasic salt. The crystals are thus allowed to grow, without change in composition, at a temperature of 25 - 40°, and are then more readily filtered.[58] Hemibasic calcium hypochlorite, $Ca(OCl)_2,0{\cdot}5Ca(OH)_2$, is formed by mixing together appropriate quantities of the compounds $Ca(OCl)_2$ and $Ca(OCl)_2,2Ca(OH)_2$ in solution. If the temperature is maintained within the range 40 - 80°, the hemibasic salt is slowly precipitated.[59,60] Processes whereby calcium hypochlorite may be crushed and finely ground (or granulated) with minimum formation of dust, have been described.[61-63]

The advantages which the true hypochlorite of calcium has over bleaching powder (see page 563) arise partly from the fact that it is free from calcium chloride, which promotes decomposition. Contamination by calcium chloride is minimized during chlorination of lime suspension by careful control of temperature and concentration, so that the hypochlorite precipitates under optimum conditions for the solubility of calcium chloride.[67] In solutions which contain calcium hypochlorite and chloride, the latter may be removed by the addition of an equivalent amount of an alkali metal salt (for example sodium carbonate or sulphate) which will produce an insoluble calcium salt. This is filtered off, and the solution evaporated, when calcium hypochlorite, free from alkali or calcium chloride, separates.[68-73] By adding calcium hydroxide to a solution of calcium hypochlorite and calcium chloride at about 40°, it is possible to precipitate a basic hypochlorite largely free from chloride.[74] Various other processes, including the addition of sodium hypochlorite or sodium hydroxide, have been suggested to remove calcium chloride, or to diminish its effects.[75,76]

The solubility of calcium hypochlorite passes through a minimum at about 0°C. In pure water the solubility is 22·7, 21·5 and 22·5% at -10°, 0° and 18° respectively. The temperature–solubility curve retains the same form on addition of calcium chloride, with a minimum near 0° for all concentrations of calcium chloride, but the solubility is much reduced in the presence of this salt.[77]

A triple salt having the formula $Ca(OCl)_2,NaOCl,NaCl,12H_2O$ is prepared by crystallizing a solution containing appropriate amounts of the ions involved, at a temperature below 16°.[78-81] The salt is unstable at higher temperatures, but is converted into a stable mixture of calcium hypochlorite and sodium chloride by treatment with calcium chloride solution at 26°. The triple salt, which may be used for bleaching purposes, is also formed on chlorinating a solution of sodium and calcium hydroxides (in the ratio 2 : 1) in a saturated sodium chloride solution.[79] Barium, strontium and calcium hypochlorites are prepared by shaking an aqueous suspension of the corresponding hydroxide with a solution of chlorine monoxide in carbon tetrachloride; evaporation of the neutral solutions in a vacuum at 40 - 45° gives the monohydrates.[28]

The hypochlorites of the transition metals have been little studied. Impure silver hypochlorite is obtained by shaking silver oxide with a concentrated solution of sodium hypochlorite at 70 - 80°,[28] and zinc hypochlorite by chlorinating an aqueous suspension of zinc oxide.[82]

Esters of Hypochlorous Acid.

Brief reference has already been made to the use of these esters in separating hypochlorites from other salts. They may be prepared by passing chlorine monoxide into alcohol,[85] or by reaction of a concentrated aqueous solution of hypochlorous acid with alcohol.[85] The tertiary compounds (e.g. *tert.*-butyl hypochlorite) are conveniently prepared by adding the corresponding alcohol to concentrated sodium hydroxide solution, and diluting with water until a homogeneous solution is obtained. The liquid is cooled with ice-water, light is excluded, and chlorine passed in. The hypochlorite separates on the surface and may be dried with calcium carbide.[84] A solution of ethyl hypochlorite may be prepared by first chlorinating water containing 20 g./litre of suspended chalk, and then filtering the solution and shaking it with carbon tetrachloride containing 2% of ethyl alcohol.[83] The alkyl hypochlorites are mobile, yellow, volatile liquids, with an irritating odour. The vapours attack the eyes and mucous membranes. The boiling points are: methyl hypochlorite, 12°/726 mm.;[85] ethyl hypochlorite, 36°/752 mm.;[85] *tert.*-butyl hypochlorite, 79·6°/750 mm.;[84] *tert.*-amyl hypochlorite, 76°/752 mm., (boiling with much decomposition).[84] The two latter hypochlorites have densities d_4^{18} 0·9583 and d_4^{25} 0·8547 respectively.[84] The stability of these esters varies widely with the nature of the alkyl group; *sec.*-alkyl hypochlorites are the least stable, *iso-* and normal primary alkyl hypochlorites are more stable, and the tertiary alkyl compounds have a high stability.[83] The primary and secondary alkyl hypochlorites decompose explosively when exposed to light, and rapidly even when light is excluded, the aldehyde or ketone being formed:-

$$R.CH_2OCl \rightarrow R.CHO + HCl$$
$$R_2.CHOCl \rightarrow R_2{:}CO + HCl.$$

Some carboxylic acids and their esters are also among the decomposition products. Decomposition is not quite so ready in the complete absence of hydrogen chloride.[86] With the tertiary alkyl hypochlorites, elimination of hydrogen chloride cannot occur, and this no doubt accounts for their stability. In strong sunlight, or on heating, decomposition occurs and an alkyl chloride is produced:-[84]

$$R_3C.OCl \rightarrow R_2C = O + RCl.$$

The esters are strong oxidizing and chlorinating agents. Like the free acid, they react with olefinic compounds, forming the chlorohydrin by addition across the double bond.[87,88]

The principles governing electrolytic processes for the production of metal hypochlorites have been discussed fully in Mellor,II,276. Later work has been concerned with operating procedure,[89-95] construction of cells,[96-101] and the influence of electrode potentials;[102-104] developments are largely technical, and need not be discussed in detail here.

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BLEACHING POWDER

Because of the widespread use of bleaching powder, the study of its chemistry has continued. Many of the general features which control its quality were discussed in the original treatise (Mellor,II,258), but some must be mentioned again since additional evidence is now available. The structure of bleaching powder, which remained a problem for so long, is now known. The main method of preparation, by passing chlorine over slaked lime, has been modified throughout the years to enhance the available chlorine content and the stability. The original method involved stacking the lime on shelves, and raking at intervals to expose a fresh surface to the chlorine; this was modified by passing chlorine up a vertical tower, while the slaked lime was moved from shelf to shelf down the tower by mechanical scrapers. Since more heat was evolved at the top of the tower, where fresh lime was exposed, it was necessary to arrange the cooling system accordingly.[1,2] If the temperature rose above 50°, an appreciable amount of calcium chlorate was formed, and 35 - 40° was a usual working temperature.[3] Laboratory scale experiments showed that the physical properties of the bleaching powder varied with the temperature of formation; below 55° the powder was finely crystalline, and readily wetted by water, but when chlorinated above this temperature, the product was not readily wetted.[18] Adequate stirring is of the greatest importance The following analysis of upper and lower layers of unstirred product indicate the possible degree of heterogeneity.[4]

	Free Calcium Oxide	Available Chlorine	Chlorine as Chloride	Water
Upper layer	10•12%	35•07%	2•07%	15•56%
Lower layer	26•65	30•69	1•31	10•01

When there is insufficient stirring during preparation, heat is evolved by the bleaching powder after packing as a result of interaction between particles of different composition.[4] More uniform composition is now obtained by allowing the lime to move, with a countercurrent of chlorine, along a rotating and nearly horizontal cylinder,[5-7] or in a vertical tower by means of a rotating screw,[8,9] or by projecting a shower of powdered lime down a high tower, up which a rapid stream of chlorine is passing.[10-12] Adequate heat control is possible by standardizing working conditions and the processes are continuous. The heat evolved in chlorination, which varies somewhat with the quality and water content of the lime, has been determined by passing chlorine over slaked lime in a vacuum-jacketed calorimeter. Using pure slaked lime having a 4% excess of water, and chlorinating to the extent of 40%, the heat evolved corresponded to 237 - 247 g.-cal. per gram of chlorine absorbed. Chlorine showed no reaction with very carefully dried calcium hydroxide.[26]

The quantity of excess water present in the slaked lime is not of major importance in determining the quality of the product. In general, variation in the range 0 - 7% has no significant effect on the rate or the extent of chlorination, although 4% is regarded as the best value. As little as 0•5% of excess water may be used. Physical uniformity is important, since any free calcium oxide is slaked during chlorination, causing local overheating,[19] and it is recommended that slaked lime be allowed to stand for some days to increase its homogeneity.[3] During chlorination however, large amounts of water are formed, as is shown by the simplified equation:-

$$Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O,$$

and the realization that this water limits the degree of chlorination has led to the production of bleaching powder having a higher available chlorine content than was possible in the normal reaction. The water may be removed in a two-stage process. Chlorination is allowed to proceed nearly to completion, and water is then removed under vacuum; this is then followed by further chlorination.[13-15,20,21] In a typical modification of this process, the reaction is first carried out at 20-25° under a pressure of 40-90 mm., when the product has 28-30% of available chlorine, and 40% of water. The second stage in the chlorination is then carried out at 50-55° under a pressure of 30-50 mm., giving a product with 36·5% of available chlorine and 0·9% water.[16] Up to 40% of available chlorine may be obtained with this type of process.[17] In other modifications the water is removed continuously, care being taken however that only a small quantity of water is removed in the early stages of chlorination.[22,23] Removal of water is usually effected by means of reduced pressure, but in some cases the heat of reaction is utilized, the water vapour being removed from the system by the stream of chlorine gas.[24,25]

Bleaching powder is well known to deteriorate on storage, and its stabilization has been the subject of much investigation.[27] Decomposition rates are highly variable, as the following data show. In samples stored in wooden casks, the available chlorine was found to decrease at the rate of 0·046% per day.[28] Other samples stored at 45° lost 50% of their available chlorine in periods varying from 2-30 weeks.[29] For samples stored in unheated conditions the loss is greater in summer, being 1·44% per month compared with 0·61% per month in winter; bleaching powder stored in the dark loses slightly less available chlorine than when stored in light.[30] On deterioration, calcium chloride, calcium chlorate and oxygen are formed.[29,32] The influence of external conditions is well illustrated by accelerated decomposition at 80-90°; when (*a*) stored as dry powder in a drum; (*b*) as dry powder in a closed bottle; (*c*) mixed with water; and (*d*) mixed with brine, the percentage losses of available chlorine were 58·8, 38·1, 14·3 and 13·1% respectively.[31]

The stability of bleaching powder is influenced considerably by the presence of other compounds in admixture. The presence of water greatly accelerates decomposition, especially at higher temperatures.[33] The removal of the bulk of the water produced during chlorination has been already referred to, final drying may be achieved at 100° at atmospheric or reduced pressure,[27,34] or by passing air or other gases at a higher temperature through the bleaching powder, the conditions being so arranged that the powder is in contact with the hot gas for a few seconds only. By observing these conditions, loss of available chlorine is negligible.[35-38] The presence of carbonates, (e.g. sodium, potassium or calcium carbonate, sodium bicarbonate), can produce rapid deterioration, since these compounds serve as sources of carbon dioxide.[41,42] It is therefore important that bleaching powder should be prepared from lime which has been fully calcined, otherwise the calcium carbonate remaining causes decomposition. A sample of bleaching powder was prepared from lime calcined at 600°, and its available chlorine content fell from 34·6% to 28% after 30 days storage. A suitable temperature for calcination of calcium carbonate is 900°. If much higher temperatures are used, reaction can occur between lime and the silica in the kiln; the chlorination of the resulting slaked lime is slower, and the bleaching powder inferior.[32] Traces of free metals (iron, magnesium, nickel, cobalt) catalyze the decomposition, sometimes explosively. The accidental introduction of organic compounds is also dangerous.[32] Ferric and manganic oxides accelerate decomposition, but aluminium and magnesium oxides and silica have little effect.[33] Addition of calcium oxide increases stability by virtue of its ability to take up uncombined water, and this represents one of the most useful industrial methods of stabilizing bleaching powder. A large excess is usually used (up to 20% of the weight of bleaching powder) and such a product is able to withstand storage under tropical conditions.[43-49] Caustic alkalis also increase stability; when lime is slaked with sodium hydroxide solution instead of water and then chlorinated, a high-quality product is obtained which may contain as much as 60% available chlorine. The high proportion of hypochlorite results from the reaction:-

$$Ca(OH)_2 + 2NaOH + 2Cl_2 \rightarrow Ca(OCl)_2 + 2NaCl + H_2O.$$[39,40]

Soda lime also increases stability, as does sodium sulphate; calcium sulphate and talc have little effect.[33,42] The stability of bleaching powder is measured by first determining the available chlorine by the well-known sodium arsenite-potassium iodide method. A sample is then well crushed, heated at 100° for two hours, and the available chlorine again determined.

Bleaching powder in current production falls into four main grades, the first three of which are stabilized:-

(*a*) Water sterilizing powder. Available chlorine 25%. Under test, the powder does not lose more than 2·5% of the original available chlorine content. The uncombined lime (expressed as CaO) and water contents do not exceed about 8%.

(*b*) Super-tropical bleaching powder. Available chlorine 30%. This grade is suitable for use in the tropics. Its stability is similar to that of (*a*).

(*c*) Tropical bleaching powder. Available chlorine 34%. This grade is useful for gas decontamination in temperate climates, and although its stability is lower than that of (*b*), it has an appreciable life under tropical conditions. Under test, its available chlorine content does not fall below about 28%.

(*d*) Unstabilized bleaching powder. Available chlorine 35%. This grade is useful for general sanitation purposes, and it is appreciably lower in stability than grades (*a*), (*b*) and (*c*).[90,91]

A wide variety of products is manufactured in which the hypochlorite content is greater than that normally obtained in the chlorination of slaked lime. The name 'bleaching powder' was intended to apply only to products prepared by this method, but as it is sometimes used to cover the products enriched in hypochlorite, these will be briefly mentioned here. Inferior bleaching powder may be improved by direct addition of pure calcium hypochlorite.[50-52] The chlorination of a calcium hydroxide suspension can give, under carefully controlled conditions, pure calcium hypochlorite. Under most conditions, however, basic salts are obtained containing a high proportion of hypochlorite, with available chlorine over 60%.[53,54] This value can readily be increased to 80%, and the conditions which give increased available chlorine content are, of course, those which favour the formation of pure calcium hypochlorite. These crystalline products are more stable than normal bleaching powder, partly because of the low chloride content.[55,60,61] In some cases the aqueous mixture obtained by chlorinating milk of lime is used directly as a bleaching solution, without the isolation of a solid product.[56] Ordinary bleaching powder may be enriched by adding water and crystallizing again. By this means the available chlorine has been increased to about 75%.[57-59]

Hydrogen peroxide solutions have also been used for crystallization.[62] A more stable form of bleaching powder can also be produced by chlorination of slaked lime suspended in carbon tetrachloride, and many modifications of this process have been described.[63-73] The water formed in the reaction may be removed by one of two methods; (*a*) by removal of carbon tetrachloride under slightly reduced pressure, followed by removal of water at a higher temperature and under vacuum, or (*b*) the removal of water and carbon tetrachloride together, at atmospheric pressure, by azeotropic distillation. The quality of the product depends upon the particle size of the slaked lime; the fractional sedimentation of the product, suspended in carbon tetrachloride, showed the available chlorine contents of the largest and smallest particles to be 31·1% and 39·1% respectively.[73]

The earliest investigations into the structure of bleaching powder showed it to contain calcium hypochlorite, calcium chloride, calcium hydroxide and water, but the exact manner in which these compounds were associated in bleaching powder remained an unsolved problem for many years. Early studies (Mellor,II,258-267) were largely concerned with the reasons for the non-deliquescence of bleaching powder, and the difficulty in carrying the chlorination process beyond about 35% available chlorine. Chemical methods were employed, and the compound calcium chlorohypochlorite, $Ca(OCl)Cl$, featured prominently in the interpretation of results. Work of this nature continued until after 1930,[74-80] and although the structure was not elucidated, the presence of calcium chlorohypochlorite was shown to be improbable.[79] Many original methods of investigation were used; for instance, bleaching powder was shown to react with metallic mercury at low temperatures to form a compound which was probably $Ca(OHgCl)_2$. All the available chlorine disappears during this reaction, so that both available chlorine atoms are probably similarly combined, (as $Ca(OCl)_2$), in bleaching powder.[80] Some very significant conclusions were reached from a study of the stable products formed in the systems, (*a*) $CaCl_2-CaO-H_2O$; (*b*) $Ca(OCl)_2-CaCl_2-H_2O$, and (*c*) $Ca(OCl)_2-CaO-H_2O$.[81] In system (*a*), the only basic salt obtainable at 0°C. was $CaCl_2,3Ca(OH)_2$ (hydrated); in system (*b*), no compound of calcium hypochlorite and calcium chloride was obtained at 0°, and in system (*c*), the two basic hypochlorites, $Ca(OCl)_2,2Ca(OH)_2$ and $Ca(OCl)_2,3Ca(OH)_2$, were isolated. The results indicated that bleaching powder may well be a mixture of basic calcium hypochlorite with basic calcium chloride. The structure was finally established in 1935, when the application of the methods of *X*-ray diffraction resulted in a complete understanding of the products of reaction and the resultant equilibria.[82,83] On the basis of phase equilibria measurements, samples of all stable products formed from the system $CaO-CaCl_2-Ca(OCl)_2-H_2O$ between 25° and 40° were isolated, and their *X*-ray and refractometric characteristics determined; the products formed during chlorination of slaked lime were then identified by these methods. The first products of chlorination are a basic hypochlorite, $Ca(OCl)_2,2Ca(OH)_2$, and a basic chloride, $CaCl_2,Ca(OH)_2,H_2O$. On further chlorination, the chlorine is taken up by the basic hypochlorite; this is thereby converted into a mixed crystal, the chief constituent of which is calcium hypochlorite. During this second stage the basic chloride is unchanged, and ordinary bleaching powder is a mixture of the basic chloride with the mixed crystal hypochlorite. The stability of this basic chloride is responsible for the non-deliquescent nature of bleaching powder, and for the resistance of the powder to further chlorination beyond 35%. When such further chlorination is achieved, the hypochlorite mixed crystal persists, but the basic chloride is partly converted to tetrahydrated calcium chloride. Crystallographic examination of the compound $Ca(OCl)_2,2Ca(OH)_2$ (hexagonal) gave the unit cell dimensions as $a_0 = 6{\cdot}305$ A., $c_0 = 6{\cdot}535$ A. For tetragonal $Ca(OCl)_2,3H_2O$, $a_0 = 12{\cdot}04$ A., $c_0 = 8{\cdot}65$ A.; there are eight molecules in the unit cell.[83] In early optical work on bleaching powder, some of the crystals were found to exhibit double refraction when the powder was moistened with tetrachloroethane, and this property varied with the composition of the bleaching powder.[74] It is now known that birefringence is a useful index of the hypochlorite content of the powder, since hypochlorite is the only strongly birefringent group present.[83]

The chemical properties of bleaching powder are those of a mixture of calcium hypochlorite, chloride and hydroxide. Three reactions are important in thermal decomposition:-[84]

$$\begin{aligned}
&(1)\ Ca(OCl)_2 \rightarrow CaCl_2 + O_2\\
&(2)\ 3Ca(OCl)_2 \rightarrow Ca(ClO_3)_2 + 2CaCl_2\\
&(3)\ Ca(OCl)_2 + CaCl_2 \rightarrow 2CaO + 2Cl_2.
\end{aligned}$$

If the bleaching powder contains a large quantity of water, (*ca.* 18%), reactions (2) and (3) predominate. As the water content is decreased, reaction (1) prevails, and the decomposition becomes explosive at 150°.[85] It provides a cheap and simple means for the production of oxygen on a small scale in industries where calcium hydroxide is a by-product.[86] Numerous examples of bleaching powder explosions have been recorded. Traces of iron and manganese oxides which occur in the limestones used as the source of lime have a catalytic effect on explosion, and the calcium chlorate present contributes to the explosion risk.[87] The smell of chlorine associated with bleaching powder is due to carbon dioxide in the atmosphere:-

$$Ca(OCl)_2 + CaCl_2 + 2CO_2 \rightarrow 2CaCO_3 + 2Cl_2.$$

The reaction is accelerated by increase in temperature and water content,[84] and may be used to free chlorine gas from carbon dioxide present as an impurity.[88] Large quantities of bleaching powder were manufactured in wartime for use as a decontaminant for vesicant war gases, particularly mustard gas; the latter is oxidized to dichlorodiethyl sulphoxide and sulphone. The reaction is strongly exothermic, and the mixture may take fire, but the vigour with which reaction occurs varies with the water content of the bleaching powder. Some fresh dry samples of bleaching powder have been found to give no apparent reaction when mixed with mustard gas, but to inflame when a few drops of water were added to the mixture.[89]

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CHLOROUS ACID AND THE CHLORITES

Chlorous acid is the least stable of the oxyacids of chlorine, and is known only in solution. Methods for the preparation of chlorous acid and its salts, e.g. by the reaction of chlorine dioxide with alkaline solutions, by treatment of sodium peroxide or hydrogen peroxide with chlorine dioxide, or by reaction between metal chlorites and mineral acids, were discussed in the original Treatise (Mellor,II,281 - 282), as was the decomposition of chlorous acid. A number of reactions in which chlorous acid and the chlorites are produced or involved have necessarily been discussed elsewhere (see page 522 et seq.). The chlorites of many metals have been prepared, usually by simple metathesis (often by reaction between a solution of the metal sulphate and barium chlorite); to avoid duplication, any particular features connected with the preparation of metal chlorites will be mentioned below when their properties are discussed. The chlorites of the alkali and alkaline earth metals, however, are especially important because of their industrial usage, and a number of methods for their large scale preparation has been developed.

The reaction of chlorine dioxide with aqueous alkali produces chlorate as well as chlorite:-

$$2ClO_2 + 2OH^- \rightarrow H_2O + ClO_2^- + ClO_3^-.$$

The formation of chlorate may be minimized by adding reducing agents to the alkali. For example, in the presence of sulphur or sodium sulphite, a high yield of sodium chlorite is obtained.[1] Alternatively, carbonaceous reducing agents may be used, such as animal charcoal, sugar,[1] coke, wood, sawdust, paper pulp,[2] or activated carbon.[3,4] Nitrogen compounds have also been used;

the addition of ammonia, or one of a range of compounds containing the $-NH_2$ or $-CN$ group, enables chlorine dioxide to be converted completely to chlorites of high purity.[5] Suitable reducing conditions are obtained if an aqueous solution of chlorine dioxide is treated with sodium amalgam, ($Na < 0{\cdot}1\%$); sodium chlorite is formed, with negligible amounts of sodium chlorate and mercuric oxide. Since the mercury cathode of an alkali chloride electrolytic cell can serve as the amalgam, this process is clearly capable of large-scale application.[6,7] The cation of a metal of variable valency, in its lowest valency state, also serves as a reducing agent. The lower oxides, hydroxides, or salts of manganese, copper, lead, cerium and iron have been found efficient for this purpose: compounds of bivalent nickel, cobalt or tin, and mercurous compounds, are less efficient. The metal compound in its higher valency state may be reduced for re-use.[8] A study of the electrochemical and thermodynamic equilibria involved in the reduction of chlorine dioxide to chlorite ion indicated that lead oxide was likely to be one of the most suitable reducing agents.[9] Even when they are not the operative reducing agents, small quantities of these metal salts are found to catalyze the formation of chlorite. For example, in a reaction using sodium formate as reducing agent, a given quantity of chlorine dioxide was not fully reduced after 3 hours, but in the presence of a few mg. of silver nitrate the same reaction was complete within 30 minutes. The free metals silver, nickel, manganese, copper, cobalt, iron, mercury and gold, and their compounds, all possess this catalytic activity.[3,10] Reduction by nascent hydrogen has also been employed; chlorine dioxide is passed into a solution and allowed to bubble over a cathode at which hydrogen is being evolved: the formation of chloric acid is much reduced, and the unstable chlorous acid immediately reacts with alkali to give the more stable chlorite.[11] There are few references to other methods of chlorite preparation. Alkali metal chlorites, free from chlorates, are produced in the laboratory by reaction beteen chlorine dioxide and the corresponding metal peroxide, e.g:-

$$2ClO_2 + Na_2O_2 \rightarrow 2NaClO_2 + O_2.$$

On a large scale it is convenient to absorb the chlorine dioxide in an aqueous solution containing hydrogen peroxide and the alkali metal bicarbonate, preferably at about 25°.[12] Because of the large differences in solubility between chlorites and other related salts, fractional crystallization provides a useful means of purifying metal chlorites.[13-17] When chlorine dioxide reacts with a solution of equivalent amounts of sodium and potassium hydroxides, the chlorate is readily crystallized from the solution as the relatively insoluble potassium chlorate. From the mother liquor the trihydrated chlorite, $NaClO_2,3H_2O$, may then be obtained by further evaporation. To prepare anhydrous sodium chlorite, the trihydrate is made into a slurry with water at 38° and the solution, saturated at this temperature, is separated and cooled to 25°, when the anhydrous salt crystallizes.[13]

Properties.

Chlorous acid is a fairly strong acid, and addition of hydrochloric acid to solutions of sodium chlorite gives approximately the pH obtained when the same quantity of hydrochloric acid is added to water. The ionization constant has been determined by titration methods, e.g. by following, with a glass electrode, the pH change as a solution of barium chlorite is treated with dilute sulphuric acid; reported values of K_{25} are[19] $4{\cdot}9 \times 10^{-3}$ and $1{\cdot}10 \times 10^{-2}$.[18] The free energy of ionization is 3151 g.-cal.[19] The heat of formation (ΔH_{298}) and free energy (ΔF_{298}) of the ClO_2^- ion are $-17{\cdot}18$ and $2{\cdot}90$ kg.-cal., respectively. Corresponding values for the acid $HClO_2$ are $-13{\cdot}68$ and $0{\cdot}23$ kg.-cal. The heat of reduction of the chlorite ion by the iodide ion has also been measured.

For the reaction:-

$$2H_2 + ClO_2^- \rightarrow Cl^- + 2H_2O,$$

$\Delta H_{298} = -159{\cdot}12$ kg.-cal.[20]

Because of its use as a bleaching agent,[21,22] the stability of sodium chlorite has been studied carefully, both in the solid state and in solution. The anhydrous salt is not hygroscopic, and samples have been kept for ten years with only slight loss. Heating for 30 minutes at 150° causes no explosion. The thermal decomposition of the solid produces no chlorine dioxide:-

$$3NaClO_2 \rightarrow 2NaClO_3 + NaCl;$$

the decomposition temperature varies with moisture content, being 202° with 3·7% of water and 177° with 10·7% of water.[21,22] The mode of decomposition of aqueous solutions is profoundly influenced by the pH of the solution. In alkaline solution sodium chlorite is stable in the absence of light, and the very slow decomposition that occurs on boiling is probably in accord with the above equation. However, for pH values less than 7, the rate of decomposition increases considerably with decrease in pH. This is illustrated in Table XVI.

The decomposition is usually written:-

$$4HClO_2 \rightarrow 2ClO_2 + HClO_3 + HCl + H_2O.$$

This involves a chlorine dioxide/chloric acid ratio of 2 : 1. Table XVI shows that this equation does not fully represent the decomposition, since this ratio is consistently higher than 2. Decomposition is very slow at pH values above 4·6. The results in Table XVII give a measure of the rate of decomposition of sodium chlorite solutions at pH 4, and the variation of this rate with concentration.[21] The decomposition of sodium chlorite in neutral solution can be accelerated by metallic catalysts; in the presence of palladium the chlorite decomposes to give chlorate and chloride, but no chlorine dioxide, and the decomposition rate increases with increase in temperature and quantity of catalyst. The passage of hydrogen through the solution has no influence on

TABLE XVI.- INFLUENCE OF pH ON THE DECOMPOSITION OF 0·25 MOLAR SODIUM CHLORITE SOLUTIONS AT 60°

pH	$NaClO_2$ decomposed after 30 minutes (molar)	Ratio $ClO_2/NaClO_3$ in products
0·6	0·25	2·4
2·0	0·247	2·3
2·2	0·232	2·1
3·2	0·165	2·1
3·8	0·041	2·4
3·9	0·024	2·5
4·6	0·006	2·1

TABLE XVII.- INFLUENCE OF CONCENTRATION ON THE DECOMPOSITION OF SODIUM CHLORITE SOLUTIONS AT pH = 4

Temperature	25°	25°	60°	60°
Initial $NaClO_2$ concn. (molar)	2·6	1·25	0·25	0·005
$NaClO_2$ (molar) decomp. in 30 minutes	0·12	0·205	0·024	0·0008
% decomposition	4·6	16	10	16

the decomposition. Platinum, gold and nickel have similar catalytic properties, but copper is less efficient.[23]

The reactions of chlorites are considerably modified in the presence of chlorine or hypochlorites. The action of chlorine on sodium chlorite is a preparative method for chlorine dioxide (see page 522). With sodium hypochlorite, the products are sodium chlorate and chlorine dioxide, in a ratio depending on the pH of the solution. Thus at pH = 2, chlorine dioxide is liberated with no evidence of chlorate formation, while in alkaline solutions chlorate is formed exclusively:-

$$NaClO_2 + NaClO \rightarrow NaClO_3 + NaCl.$$

On mixing sodium chlorite and hypochlorite solutions at pH values of about 5 - 6, the initial reaction is:-

$$HClO_2 + HClO \rightarrow 2ClO_2 + HCl + H_2O.$$

On standing, the chlorine dioxide can react further with excess hypochlorous acid:-

$$2ClO_2 + HOCl + H_2O \rightarrow 2HClO_3 + HCl.$$

The rate of this reaction varies with pH, and is increased at high temperatures and pressures. In view of these successive reactions, the relative amounts of chlorate and chlorine dioxide produced depend also on the chlorite : hypochlorite ratio of the reactants. When this ratio is 2 : 1, chlorine dioxide predominates, since excess hypochlorous acid is not available for chlorate formation. On increasing the ratio beyond 1 : 1, immediate chlorate formation occurs and the quantity of chlorine dioxide decreases, while with a ratio of 1 : 4 the chlorine dioxide is completely converted to chlorate within 30 minutes at room temperature.[21]

The action of certain reducing agents, such as aldehydes, on sodium chlorite yields chlorine dioxide; this has already been discussed. With iodides, iodine is first liberated, and since chlorites are able to oxidize iodine to iodate ion, the reaction is:-

$$3HClO_2 + 2I^- \rightarrow 2IO_3^- + 3HCl.$$

This reaction forms the basis of the analytical determination of chlorites[24] (see page 672). The solutions may be standardized by adding acetic acid and excess of potassium iodide, and titrating the liberated iodine. The solution is buffered to a pH of between 5·3 and 5·7. If the pH is below 5·2, some loss by chlorine dioxide evolution occurs. At pH values above 6·0, the reaction is too slow to be of value. Standard sodium chlorite solutions may be used in the volumetric determination of sulphur dioxide and sulphites.[25,26] Solid sodium chlorite and sulphur will ignite if mixed together and moistened, and vulcanized rubber contains enough sulphur to cause obvious reaction on contact with moist sodium chlorite.[22] Oxidizing agents, if sufficiently strong, will oxidize chlorite to chlorate. In neutral solution, oxidation by potassium permanganate proceeds according to the equation:-

$$3ClO_2^- + 2MnO_4^- + H_2O \rightarrow 3ClO_3^- + 2MnO_2 + 2OH^-.$$

The reaction stops when an appreciable amount of alkali has been produced, indicating that it is probably the acid $HClO_2$, rather than the ion ClO_2 , which undergoes oxidation. In the presence of a calcium, magnesium or zinc salt, which is able to neutralize the alkali or precipitate it from the solution, the reaction proceeds to completion.[27] The oxidation and reduction of chlorites in electrolytic cells has been studied by determining the e.m.f. of a number of cells in which potassium or calcium chlorite was one of the electrolytes. Many variations in the second electrolyte were tried, and numerous voltage changes have been recorded.[28,29]

The chlorites of the alkali metals are obtained in pure form by reaction of the corresponding sulphate with barium chlorite. When saturated solutions of sodium sulphate and barium chlorite are mixed and concentrated in a vacuum at 10 - 15°, the trihydrate, $NaClO_2,3H_2O$, separates out as lustrous plates which are strongly birefringent and explode on percussion.[30] The crystals are triclinic, with $a:b:c = 0{\cdot}4041:1:0{\cdot}6353$, and $\alpha = 103°43{\cdot}5'$, $\beta = 119°3'$ and $\gamma = 81°46{\cdot}5'$.[31] The chlorites of potassium, rubidium and cæsium are biaxial, and not isomorphous with the ammonium salt; the potassium and rubidium chlorite crystals are alike, but differ from the cæsium salt.[32] Lithium chlorite is prepared by a similar method, and gives crystals which are highly deliquescent. Unlike sodium chlorite, the lithium salt is not precipitated from aqueous solution by the addition of alcohol or ether.[30]

When ammonium sulphate and barium chlorite in equivalent amounts react in concentrated solution at 15 - 20° the filtrate on evaporation in a vacuum gives ammonium chlorite as long transparent needles.[33] The salt is tetragonal, with axial ratio $1:0{\cdot}420$, and $a = 8{\cdot}95$ A. There are 4 molecules in the unit cell, and the positions of the NH_4 group and Cl and O atoms have been defined. The calculated density is 1·90.[32] Sulphur dioxide reduces ammonium chlorite to the chloride. The same method of preparation applied to mono-, di- and trimethylammonium sulphates gave solutions of the corresponding chlorites which were very unstable, the stability decreasing with degree of substitution, and they could not be crystallized. However, tetramethylammonium chlorite can be separated as colourless crystals by this method. The salt is deliquescent, has a neutral reaction in aqueous solution and, unlike ammonium chlorite, explodes on percussion.[33] Hydrazine chlorite has been prepared by suspending a known amount of hydrazine sulphate in a little water, and adding 0·5 equivalents of barium hydroxide. Barium chlorite (0·5 equivalent) is then added slowly at 0 - 2°. After rapid filtration, the solution is poured into alcohol at -10°, when crystals of hydrazine chlorite ($N_2H_4,HClO_2$) separate. The salt is spontaneously inflammable when dry. Attempts to isolate the dichlorite, $N_2H_4,(HClO_2)_2$, as a solid were not successful. The stability of solutions of hydrazine chlorite is influenced by pH. Thus if a solution containing hydrazine hydrochloride and sodium chlorite is boiled, the reaction:-

$$N_2H_6Cl_2 + 2NaClO_2 \rightarrow N_2 + NaCl + 2H_2O + 2HCl$$

is quantitative, whereas if pure hydrazine hydrate is used, no nitrogen is evolved.[34] Decomposition of solutions containing hydroxylamine and chlorites is much more vigorous and prevents isolation of hydroxylamine chlorite. In neutral solution the reaction is:-

$$NH_2OH,HCl + NaClO_2 \rightarrow NaCl + \tfrac{1}{2}Cl_2 + NO + 2H_2O,$$

but with excess of the hydroxylamine salt nitrous oxide is a reaction product:-

$$2NH_2OH,HCl + NaClO_2 \rightarrow NaCl + N_2O + 3H_2O + 2HCl.^{34}$$

Despite an earlier failure to prepare magnesium chlorite by reaction of magnesium sulphate with barium chlorite,[30] the compound may be obtained by this method if the solution is allowed to evaporate slowly in air over several days, when the hydrate $Mg(ClO_2)_2,6H_2O$ separates.[31] The crystals are tetragonal; $a = 10{\cdot}29$ A., and $c = 10{\cdot}55$ A. The experimental and calculated density values are 1·619 and 1·593.[36] The preparation of calcium chlorite from barium chlorite and calcium sulphate is not practicable because of the low solubility of the latter. The salt is readily prepared, however, by a number of the methods mentioned earlier. Pure samples may be prepared by treating a calcium peroxide suspension with chlorine dioxide. From this solution calcium chlorite may be crystallized by evaporating in a vacuum over

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potassium hydroxide, or precipitated by adding alcohol or ether. Strontium chlorite is prepared similarly.[30] Calcium chlorite shows double refraction; the crystals are pseudocubic with two molecules in the unit cell, and $a =$ 5·8 A.[32]

Thallium and lead each form a chlorite. The thallium compound is not very stable;[30] the lead compound is more stable, and in contrast to the alkali and alkaline earth chlorites, has a low solubility in water (0·035 g. per 100 g. of solution at 0°). It has detonator properties, but its behaviour is somewhat unpredictable. The crystals are pseudotetragonal; $a:c = 1:1{\cdot}51$ and $a =$ 4·14 A. The unit cell contains one molecule, and the observed and calculated densities are 5·10 and 5·30 respectively.[32] Lead chlorite forms double salts with lead chloride and lead bromide, $Pb(ClO_2)_2,PbCl_2$ and $Pb(ClO_2)_2,PbBr_2$, but the corresponding iodide could not be prepared. The double salts are more soluble than either component. *X*-Ray analysis showed that the compounds $PbCl_2,2Pb(ClO_2)_2$ and $PbO,4PbCl_2,6Pb(ClO_2)_2$, previously believed to exist, are not in fact formed, and are merely the double salt with excess of chlorite or chloride.[37]

Little is known of the chlorites of the elements in the early Transition groups. From a solution of erbium sulphate, treated with barium chlorite and a little barium hydroxide, pale red erbium chlorite, $Er(ClO_2)_3,4H_2O$, can be separated by adding alcohol.[38] Nickel chlorite is obtained with difficulty by fractional crystallization at low temperatures of a nickel sulphate–barium chlorite filtrate. Early fractions contain basic nickel chlorite, but the hydrate $Ni(ClO_2)_2,2H_2O$ is ultimately obtained. The salt does not explode easily on percussion, but explodes when heated to 100°. The difficulty of preparation is the result of its high solubility in water and of the readiness with which its solutions deposit higher oxides of nickel.[38] The formation and properties of cupric chlorite resemble those of the nickel salt. When molar solutions of copper sulphate and barium chlorite were mixed, filtered and put aside for 24 hours, about one third of the copper present separated as a basic chlorite.[39] On treating the filtrate with excess of alcohol, the simple salt $Cu(ClO_2)_2$ was precipitated as a yellow-brown solid which decomposed in the dry state within 12 days, and exploded violently on percussion. Reaction of a copper sulphate solution with an equivalent amount of sodium chlorite gave a basic cupric chlorite, $Cu(ClO_2)_2,3Cu(OH)_2$. By mixing solutions of the constituents concerned, a number of double salts of copper have been prepared, viz. potassium cupric chlorite, $Cu(ClO_2)_2,2KClO_2,2H_2O$, cupric chloride potassium chlorite, $CuCl_2,KClO_2$, and the corresponding rubidium, cæsium and ammonium compounds.[39] The double salts $2Cu(ClO_2)_2,Mg(ClO_2)_2,8H_2O$ (brown crystals, yellow by transmitted light), $Cu(ClO_2)_2,Ba(ClO_2)_2,4H_2O$ (yellow crystals with green fluorescence), and $Cu(ClO_2)_2,TlClO_2,2H_2O$ (red-brown powder) are also known. These double salts are usually more stable than cupric chlorite.[38] Silver chlorite was one of the first heavy metal chlorites to be isolated and, like lead chlorite, it has a low solubility in water, (0·17 g. per 100 g. of solution at 0°; compare barium chlorite 30·5 g.). The salt forms pseudotetragonal crystals, $a:c = 1:0{\cdot}55$, and $a = 12{\cdot}17$ A.; the unit cell contains 16 molecules. The measured density is 4·30.[32] Some thermodynamic constants for silver chlorite are now known. The heat capacity was measured from 15° to 300°K., and the entropy calculated as 32·16 ± 0·2 g.-cal./degree/mol. at 298·1°K. From solubility measurements the thermodynamic equilibrium constant was determined, and thence the free energy of solution calculated as 4380 ± 100 g.-cal./mol. at 298·1°K. The heat of solution at 25°C. is 7200 ± 100 g.-cal./mol., and $\Delta S = 9{\cdot}5 \pm 0{\cdot}5$ g.-cal./degree/mol. at 25°C. The entropy of the chlorite ion is 24·1 ± 0·5 g.-cal./degree/mol. at 25°.[40]

Cadmium chlorite, $Cd(ClO_2)_2,2H_2O$, is monoclinic, pseudocubic, with $a:b:c = 1{\cdot}245:1:1{\cdot}371$, $\beta = 90°18'$ and $b = 7{\cdot}12$ A.[32] Both the cadmium salt and the zinc salt ($Zn(ClO_2)_2,2H_2O$) are prepared by the usual metathesis, and are isomorphous.[32,39] They do not form double salts as readily as does cupric chlorite. Further work on the chlorites of mercury has shown that the red precipitate obtained on adding not more than 0·5 equivalents of mercuric nitrate to sodium chlorite in aqueous solution is the explosive mercuric chlorite, $Hg(ClO_2)_2$. This precipitation may be used (see page 672) for the analytical determination of chlorite in the presence of other oxyacid ions of chlorine.[41] When allowed to stand in a moist condition, mercuric chlorite decomposes to the basic chloride, $HgCl_2,2HgO,12H_2O$; when boiled in water, the compound $HgCl_24HgO$ is formed. The products obtained when mercuric chlorite is treated with aqueous ammonia depend upon the relative quantities of the reactants. Three different products are known to be formed, but the product best established has the empirical formula, $Hg_2ONH_2ClO_2$.[38] Sodium chlorite gives with mercurous nitrate solutions the cream coloured unstable precipitate, $2HgClO_2,HgO,5H_2O$. The normal mercurous chlorite is yellow.[38]

Some broad analogies between the chlorite and nitrite ions can be drawn, for example by comparing the ability of each ion to act both as an oxidizing and as a reducing agent. This analogy does not extend to a similar ability to enter into co-ordination complexes, since attempts to prepare cobaltammine complexes with the chlorite group in the complex were unsuccessful. As an unstable anion is known to be stabilized by salt formation with a large cation, it is not surprising that salts such as hexamminocobaltic chlorite, $[Co(NH_3)_6](ClO_2)_3,H_2O$, and chloropentamminocobaltic chlorite, $[Co(NH_3)_5Cl](ClO_2)_2$, were isolated in this work.[42] A certain similarity between the chlorites and the iodides may be observed on comparing the solubilities and chemical properties of the corresponding silver, lead and mercury compounds.

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CHLORIC ACID AND THE CHLORATES

Preparation.

Free chloric acid is known only in aqueous solution, and its solutions are commonly prepared from barium chlorate solution by adding sulphuric acid, filtering the solution, and evaporating. Decomposition commences at concentrations above 40%; at room temperature the products are oxygen and chlorine, while some perchloric acid is formed at higher temperatures. The chlorates of the alkali and alkaline earth metals continue to be of commercial importance; they are prepared either by the action of chlorine on the alkali, or by electrolytic oxidation of the chloride. The latter process has largely superseded the former, but the patent literature shows that the former method can certainly not be regarded as obsolete. The basic principles underlying these methods have been described earlier (Mellor,II,303); the more recent work here outlined has been concerned primarily with the influence of experimental conditions and technique on the efficiency of these processes.

The overall equation for the chlorination of milk of lime is:-

$$6Ca(OH)_2 + 6Cl_2 \rightarrow Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O.$$

In the early stages of the process calcium hypochlorite is produced, and further chlorination gives rise to chlorate by the reaction:-

$$ClO^- + 2HOCl \rightarrow ClO_3^- + 2HCl.$$

For this reason it is important that there should be excess of chlorine. If the absorber vessel containing the milk of lime is air-cooled only, the temperature rises uniformly up to the last few minutes, when there is a sudden rise in temperature accompanying the conversion of hypochlorite into chlorate.[1] A temperature of 30° has been found suitable, and with water cooling and efficient stirring, a yield of calcium chlorate within 2% of the theoretical is possible.[1] If chlorination is carried out at temperatures above 40° some hypochlorite decomposes to give chloride and oxygen;[6] at 95-100° the chlorate yield falls to 65%.[1] The presence of calcium carbonate in the milk of lime should be avoided, since higher temperatures are required for its chlorination. If pure chlorine is used as the gas stream there is a danger of the formation of explosive mixtures of chlorine, hydrogen and oxygen. This can be avoided by diluting the chlorine with air to a chlorine concentration of 25-35%. The presence of charcoal is found to facilitate the conversion of hypochlorite into chlorate.[1] Using milk of lime samples containing 200 to 330 g. of lime per litre, the time required for chlorination was found to be approximately proportional to the concentration, and variation in the rate of flow of the chlorine had relatively little effect on the chlorate yield. A temperature in the range 25 - 40°C. was again found suitable for chlorate production.[2] The chlorination of magnesium oxide suspensions gives magnesium chlorate under broadly similar conditions, but the reaction temperature may be raised to 60°. Suspensions should not contain more than 170 g. of magnesium oxide per litre, otherwise the suspension thickens during chlorination, and foaming occurs, which impedes the absorption of chlorine.[7] Chlorination to zinc chlorate has also been used in the recovery of zinc salts used in paper making.[33]

The corrosion caused by solutions of chlorides and chlorates[3] has led to the use of such materials as cement, sand, kieselguhr and their mixtures for lining vessels used in these processes.[4] Chloride solutions are more corrosive than chlorates in iron or copper vessels, and the mixed solutions have a greater corrosive power than would be predicted from the additive effect of the two components. On immersion in a calcium chloride-potassium chlorate solution for 10 days at 100°, copper was found to lose 3·6, and iron 950, grams per square metre. The corrosive effect can be greatly reduced (to about one hundredth) by adding to the solution 0·125 gram equivalents per litre of sodium hydroxide.[5]

Precise conditions for the efficient preparation of the chlorates of many metals by chlorination of their hydroxides are not known. With the less common or more expensive metals it is therefore customary to prepare the chlorates by metathesis of a simple salt of the metal with the chlorate of a common metal.[8] This avoids the simultaneous production of the chloride of the metal as a by-product, and the solubilities of the salts are usually sufficiently different to permit separation by crystallization. Sodium, potassium, calcium and magnesium chlorates are particularly useful as starting materials, and for this purpose the chlorination of sodium carbonate is said to be simpler and more economical than chlorination of lime.[9] Sodium carbonate solutions react with chlorine in two ways. The first stage is represented thus:-

$$Na_2CO_3 + Cl_2 + H_2O \rightarrow NaHCO_3 + NaOCl + HCl,$$

and this reaction proceeds until all the carbonate is converted into bicarbonate. The latter is then chlorinated:-

$$6NaHCO_3 + 3Cl_2 \rightarrow NaClO_3 + 5NaCl + 3H_2O + 6CO_2,$$

and excess chlorine converts the hypochlorite formed in the first stage to chlorate. Chlorination of a solution of 200 - 300 grams per litre of sodium carbonate at 60° gives an almost theoretical yield of sodium chlorate, which is not adversely affected by prolonged chlorination.[11] The reaction with potassium carbonate follows a similar course.[10] The process also appears to proceed satisfactorily in the presence of limited quantities of water; alkali metal chlorates are prepared by chlorination of the metal carbonate containing only 3 - 20% of its weight of water at 60 - 80°. The solid product may be used directly for such purposes as weed killing, or pure chlorate may be obtained from the product by leaching, evaporating and crystallizing.[12,13] Bicarbonates can also be used in this way.[12,14] Although the presence of calcium carbonate is inconvenient in the chlorination of milk of lime, the alkaline earth carbonates can be used as starting materials if the experimental conditions are suitable; conversion to chlorate occurs when the carbonate contains about 5% of water, and is treated with chlorine at 70 - 90°.[15]

From the chlorate-chloride mixtures which result from these chlorination reactions, pure chlorates are usually obtained by fractional crystallization. If the solubility values are not suitable, they can be influenced by the addition of other salts to the solutions.[16,20-24] In calcium chlorate-calcium chloride mixtures, the former crystallizes as the dihydrate from solutions in which the chloride–chlorate ratio is between 2 : 1 and 1 : 1. The solution used should be saturated with respect to calcium chlorate dihydrate at a temperature below 60°.[17,19] If the solution is saturated with calcium chlorate (but unsaturated with calcium chloride) at temperatures above 60°, and will crystallize above this temperature, calcium chlorate is obtained as the anhydrous salt.[18] No double salts of calcium chlorate and calcium chloride are formed in this system.[25] The chloride content of a solution of these two salts (rich in chloride) may be reduced by adding calcium hydroxide in an amount slightly in excess of that equivalent to the chloride concentration: the basic salt, $CaCl_2,Ca(OH)_2,H_2O$, is formed almost instantaneously at 60° and being insoluble it may be filtered off.[26] When the chloride content of the mixture is low, addition of excess calcium hydroxide produces a basic calcium chlorate.[27] The chlorates of magnesium, calcium, barium and strontium may be extracted with acetone from mixtures containing the chlorides and/or chlorites of these metals.[28,29] In many processes, cyclic and otherwise, it is advantageous to arrange concentration and temperatures so that evaporation of solutions is not necessary to effect crystallization.[30-32] For example, the concentration of a strong solution of sodium hydroxide can be so arranged that on treatment with excess chlorine at 100° the sodium chloride produced in the reaction is precipitated. This is filtered from the hot solution, and when the filtrate is cooled to 8 - 10°, the sodium chlorate which crystallizes contains as little as 1% of sodium chloride.[31] Sodium chlorate and chlorite can also be separated in this manner. When the mixture produced by the action of chlorine dioxide on sodium hydroxide is crystallized at 30°, sodium chlorate is separated; the solution is then diluted and cooled to 5°, when sodium chlorite trihydrate crystallizes.[32]

Electrolytic Preparation.

Various aspects of the well-known method involving electrolysis of the metal chlorides have been examined in greater detail. The initial product is hypochlorite, formed by reaction between chlorine from the anode and the alkali or alkaline earth hydroxide produced at the cathode. If the solution is alkaline the hypochlorite is chemically stable, and conversion to chlorate occurs by anodic oxidation:-

$$6ClO^- + 3H_2O + 6\oplus \rightarrow 2ClO_3^- + 4Cl^- + 6H^+ + 3O.$$

The process is inefficient since evolution of oxygen represents a loss of energy. If the solution is acid, conversion to chlorate can take place by the more efficient route:-

$$2HOCl + OCl^- \rightarrow ClO_3^- + 2HCl,$$

and this is to be preferred. The electrolyte may be acidified during electrolysis to maintain the desired pH value.[34,35] For electrolysis of sodium chloride solutions, an optimum pH value between 5·9 and 6·1 has been quoted.[36] If the solution is too strongly acid, hypochlorite formation is prevented by the absence of hydroxyl ions. Careful temperature control is necessary. Both the electrode processes and the electrolyte reactions are sensitive to temperature, and high temperatures tend to decompose the hypochlorite with evolution of oxygen. The temperature for maximum efficiency varies with the electrolyte used and with the electrolysis conditions, and has to be determined in a rather empirical way. Using sodium chloride as electrolyte, efficiency is highest at 35°,[38] and electrolysis of calcium chloride solution should be carried out at a temperature below 40°.[39] A saturated solution of the chloride is usually recommended as electrolyte, the saturation being maintained by adding chloride during the electrolysis.[35,37,40-42] High current densities are desirable, and cells employing 0·015,[34] 0·5[35] and 0·1 - 0·2[36] amp./cm.[2] have been described. Current efficiency is said to be improved if the electrolyte flows continuously through a series of cells.[42,43,48-50] It is advisable to sweep through the apparatus with air, since the accumulation of hydrogen and oxygen may cause an explosion.[56,57] The addition of a small quantity of potassium dichromate to avoid reduction of hypochlorite at the cathode has been widely advocated.[35,37,39-41,51-53] In the electrolysis of the alkali metal chlorides, the use of a chromium plated cathode is said to render the addition of dichromate unnecessary. A rough deposit of chromium, (plated on iron, nickel or copper) gave more satisfactory results than a polished layer, and with this rough deposit the cathodic reduction was as little as when dichromate was added to the electrolyte. Using a chromium plated cathode, cathodic reduction was least[54] at a current density of 0·15 amp./cm.^{2} In the electrolytic preparation of barium chlorate, the addition of a little calcium chloride minimizes cathodic reduction.[55] Many electrode materials have been tested. As cathodes, carbon,[35,41,46,52] iron,[40,43,44] platinum,[36] and copper[35] have been used, and their influence on efficiency compared. As anodes, graphite and magnetite have been recommended.[43-46] The latter is said to be more efficient.[47] For a given current consumption, platinum anodes have been found to give the highest yield of chlorate.[34,36,45]

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THE PROPERTIES OF CHLORIC ACID AND ITS SALTS

Little recent work has been done on the physical properties of chloric acid, doubtless because it is available only in dilute aqueous solution and its decomposition makes accurate physical studies unprofitable. In solution in methyl or ethyl alcohol the acid is also unstable, and measurements of the electrical conductivity of the solutions were unsatisfactory for this reason.[1] The chlorate ion is more stable and has been studied in a number of crystalline salts and in neutral or alkaline solution. Its shape is that of a shallow pyramid with the chlorine atom at the apex, the fourth tetrahedral bond position being occupied by the unshared electron pair. This structure is consistent with Raman and infra-red spectra.[2] The thermochemical radius of the ClO_3^- ion is near 2·0 A., but the values calculated from the lattice energy of salts increase, over a range of about 2%, with the size of the associated cation. For rubidium chlorate, r = 1·98 A., and in the compound $[Ni(H_2O)_6](ClO_3)_2$, r = 2·05 A. This is explained by assuming that a smaller cation is able to penetrate more deeply into the field of the anion. The calculated value of the heat of formation of the gaseous chlorate anion is 57·8 kg.-cal./mol.;[3] at 25° the entropy S, = 39·3 g.-cal./degree/mol., and ΔF = 3·7 kg.-cal./mol. For potassium chlorate, S = 34·17 g.-cal./degree/mol.[4]

For the diamagnetic susceptibility of the chlorate ion a value of $-30{\cdot}2 \times 10^{-6}$ c.g.s. units has been given,[5,6] though a more recent determination gives $-24{\cdot}86 \times 10^{-6}$, with values of $-33{\cdot}27$, $-36{\cdot}81$ and $-87{\cdot}44$ (all $\times 10^{-6}$) for the susceptibilities of anhydrous sodium chlorate, potassium chlorate and barium chlorate respectively.[7] Ions of the type XO_3 often show magnetic anisotropy, which is detected by oscillating the crystals about different axes in a uniform magnetic field. Nitrates, carbonates and chlorates exhibit considerable magnetic anisotropy (whereas sulphates are almost completely isotropic) and the optical and magnetic axes are coincident. The diamagnetic susceptibility of the chlorate ion is a minimum along the axis of symmetry, whereas for nitrate and carbonate ions it is a maximum along this axis.[8,9] The Faraday effect (rotation of the plane of polarization of light under the influence of a magnetic field) has been examined for the sodium D-line for chlorates (and

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other salts) in aqueous solution.[10,11] The magneto-rotation constant is given by:-

$$\Phi = Mnw\lambda^2/s(n^2 + 2)^2;$$

w being the Verdet constant (the angle of rotation in a field of 1 gauss for 1 cm. of liquid), for light of wave-length λ, and n, s and M being refractive index, specific gravity and molecular weight respectively. The constant for the acid or salt is the sum of constants for the constituent ions, and the constants for chloric acid and its common salts may be calculated from the following values:-

Ion	$\Phi \times 10^{14}$
ClO_3^-	6·06
H^+	-1·41
Na^+	-0·23
K^+	0·61
Ca^{2+}	-2·06
Ba^{2+}	0·52

Ionic velocities in systems containing the chlorate ion have been studied.[12,13] From conductivity measurements, the anion conductance of the ClO_3^- ion at 25° is 64·58 $ohms^{-1}$; the value decreases with increase in the size of the halogen atom in XO_3^- ions, since the bromate and iodate ion conductances are 55·84 and 40·75 $ohms^{-1}$ respectively.[14] (Compare also NO_3^- = 61·62 and $\frac{1}{2}CO_3^{2-}$ = 60 $ohms^{-1}$). Conductivity measurements give a value of 0·6 for the dissociation constant of silver chlorate.[14]

The distribution of the chlorate ion between water and ethyl alcohol has been measured. In this system it is necessary to add high concentrations of another electrolyte to create a two-layer system. Using potassium carbonate for this purpose, the distribution coefficient of the chlorate ion is 2·1 (compare SO_4^{2-} = 140 and NO_2^- = 2·2). Using ammonium sulphate, the chlorate coefficient falls to 0·43 (compare NO_3^- = 0·50). The differences are attributable to variation in anion hydration.[15] Distribution measurements between water and alcohols have been used also to determine the variation in hydration of salts with the number of oxygen atoms in the chlorine oxyacid ions; the entry of oxygen into the anion appears to reduce the degree of hydration, as shown by the following values of apparent hydration numbers:-[36]

$BaCl_2$ = 12·87 $Ba(ClO_3)_2$ = 3·77 $Ba(ClO_4)_2$ = 2·004
$NaCl$ = 14·53 $NaClO_3$ = 10·44 $NaClO_4$ = 6·42

The ratios of the activity coefficients of these ions in methyl alcohol and water ($f_{MeOH}/f_{H_2O} = r$) also differ. Taking an arbitrary value $r = 100$ for the chloride ion, the ratio for the ClO_3^- ion is 46.[17]

Isotope exchange reactions involving the chlorate ion show some interesting features. Using a heavy chlorine isotope, no exchange was found to occur between the chloride and chlorate ions in solution, and this is therefore to be regarded as an irreversible oxidation-reduction system.[18] Using water containing the ^{18}O isotope, complete exchange of this isotope between water and the chlorate ions in a dissolved chlorate was observed, provided that the solution was acid, but no exchange occurred in neutral or alkaline solution.[19] Addition of hydrochloric acid to a sodium chlorate solution brings about complete exchange of heavy oxygen in 10 hours at 100° [20,21] These observations are consistent with the known differences between the chemistry of chloric acid and the chlorate ion. The greater stability of perchloric acid compared with chloric acid is reflected in the fact that no measurable exchange between water and the perchlorate ion occurs even in acid solution.[19]

Thermal Decomposition.

Chlorates of strongly electropositive metals can disproportionate on heating into perchlorate and chloride, e.g. $4KClO_3 \rightarrow 3KClO_4 + KCl$. This reaction occurs to a decreasing extent as the electropositive character of the metal is decreased. There are alternative modes of decomposition which depend upon the relative stabilities of the oxide and chloride of the metal. Thus alkali, alkaline earth and silver chlorates give the chloride of the metal and oxygen; cobalt, copper and zinc chlorates give mainly metal oxide and chlorine, while nickel, cadmium and lead chlorates give mixtures of chloride and oxide and evolve chlorine and oxygen. The influence of catalysts on the thermal decomposition of sodium and potassium chlorates (particularly the latter) has been widely investigated. Added metal oxides facilitate decomposition into metal chloride and oxygen at the expense of disproportionation, Free metals also act as catalysts, and ultra-violet light is said to promote catalyzed decomposition at room temperature.[22]

The melting and decomposition temperatures of pure sodium chlorate are 256° and 350° respectively, corresponding figures for potassium chlorate being 356° and 364°.[23,24] The temperatures at which the chlorate ion becomes unstable are similar, although the melting points of the salts differ widely. Mixtures of the two salts melt at lower temperatures and so are convenient for oxygen production, though the composition for minimum melting point (75 $NaClO_3$ - 25$KClO_3$) does not coincide with the composition for minimum decomposition temperature (15$NaClO_3$ - 85$KClO_3$).[23] The temperatures for decomposition of these salts, or their mixtures, are lowered considerably by addition of many types of catalysts; the lowering is about 70° for silica, 60° for potassium chloride and as much as 180° for manganese dioxide.[25] Potassium chloride accelerates both disproportionation and oxygen evolution reactions. With the former, the velocity coefficient k is given by the equation $k = (dy/dt)/c(a-x)$, where dy/dt is the instantaneous velocity, and c and $(a-x)$ the concentrations of potassium chloride and chlorate; the reaction is autocatalytic. The latter reaction is unimolecular, and the logarithms of the velocity coefficients when plotted against $1/T$ (in the range 400 - 500°) give straight lines.[26] The decomposition temperature of potassium chlorate is also lowered by adding oxidizing agents such as ammonium dichromate or persulphate; the process may involve mutual autoreduction.[27] The velocity of decomposition of potassium chlorate in the presence of manganese dioxide depends on the quantity of catalyst present.[24] Although the view has been challenged,[28] there seems to be ample evidence that the temperature at which a mixture of potassium chlorate with manganese dioxide undergoes spontaneous decomposition also depends upon the proportions involved, and that there is a decomposition temperature characteristic of each mixture.[29] On spontaneous decomposition the reaction is sufficiently rapid to be thermally self-supporting. With manganese dioxide catalyst the minimum temperature is 292°, and the proportions $KClO_3 : MnO_2 = 2 : 1$. Ferric oxide is also a catalyst (though less efficient than manganese dioxide) and requires a minimum temperature of 324°.[30-32] Ferric oxide exerts a promoter action when mixed with manganese dioxide, since the mixture is a more powerful catalyst than either oxide used alone.[30] This accounts for the efficiency of pyrolusite as catalyst in this reaction. Cupric oxide can also act as a promoter.[33]

Variation in pressure has a marked effect on the catalyzed decomposition of potassium chlorate. Using manganese dioxide as catalyst, the effect has been studied over the pressure range 0·01 cm. of mercury to 500 atm., and the temperature range 70° to 350°. At 126°, oxygen is not evolved from the 2:1 mixture at atmospheric pressure but is evolved at pressures below 0·01 cm. of mercury. At 175° oxygen is evolved at a pressure of 2 - 3 mm. At 320° the mixture decomposes spontaneously at atmospheric pressure, but 90% remains undecomposed after seven hours at pressures above 300 atm. Even at 500 atm. pressure of oxygen, no recombination of potassium chloride and oxygen occurs at any temperature, so that if the reaction:-

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

can be regarded as reversible, the equilibrium pressure of oxygen is in excess of this value.[35-37]

The catalytic activities of a number of metal oxides have been compared by determining the rate of oxygen evolution from mixtures (10 parts potassium chlorate to 1 part of catalyst) heated at 275°. The oxides fall in the following order of decreasing catalytic activity: Co_2O_3, Cr_2O_3, MnO_2, Fe_2O_3, Ni_2O_3, CuO, TiO_2. Using the metal sulphates as catalysts in similar experiments, the order of decreasing activity was: Cr, Co, Mn, Ti, Fe, Ni, Cu, V.[38]

These results may give some indication of the mechanism of catalysis, which has not yet been definitely established. Attempts have been made to explain the mechanism in general terms, such as electron disturbance,[39] but this cannot be readily tested by experiment. Observations on the thermal decomposition of single crystals of potassium chlorate indicates that such decomposition starts from nuclei on the surface, but this gives no guide to catalyzed decomposition.[40] The formation of some form of intermediate compound seems highly probable. When mixtures of potassium chlorate with either manganese dioxide or the cobalt oxide Co_3O_4 were heated at temperatures a little below those for spontaneous decomposition, the magnetic susceptibilities of the mixtures determined experimentally were appreciably less than values calculated by applying the additivity law to the mixture. This was interpreted as providing definite evidence for intermediate compound formation.[41,42] It is unlikely that the same mechanism applies to all examples of catalysis, but it is significant that, broadly speaking, the most efficient oxides are those of metals having a range of available valency states; the intermediate compound probably involves a valency state higher than that in the added oxide, and the manganate or permanganate ion may be important in manganese dioxide catalysis. A comparison of the efficiencies of various oxides or salts of the same metal, in which the metal displayed a range of valency states, would probably throw more light on the problem.

Oxidizing Properties.

In most of their chemical reactions the chlorates act as oxidizing agents and are reduced to chlorides. Many chlorates react vigorously with sulphur, the readiness of reaction increasing as the electropositive character of the metal decreases. The presence of a trace of water is necessary; this permits the formation of sulphuric acid and thus the liberation of chloric acid.[43,46] The dry mixtures may be preserved indefinitely. The chlorates of the following metals are arranged in order of increasing readiness to react with sulphur: barium, strontium, calcium, lead, copper, chromium, magnesium, nickel, cobalt, zinc, cadmium. At temperatures below 50-60° some chlorine dioxide is evolved, and higher temperatures give a mixture of chlorine and oxygen. The sulphur is oxidized ultimately to sulphate, and sulphur monochloride is believed to be one of the intermediate products.[43] Reaction under these conditions is much slower with the alkali metal chlorates, although addition of sulphuric acid renders the mixture explosive in all cases.[44] Ignition temperatures of mixtures of sulphur with some chlorates are: lead chlorate, 63-67°; silver chlorate, 74°; barium chlorate, 108-111°; potassium chlorate, 160-162°.[45] The oxidation of sulphur, selenium and tellurium does not present a regular progression, since selenium is oxidized more readily but tellurium less readily than sulphur. A slightly moist mixture of selenium with any chlorate, except those of the alkali metals, becomes incandescent.

Chlorates of the ammine complexes, e.g. $[Zn(NH_3)_4](ClO_3)_2$ and $[Cd(NH_3)_6](ClO_3)_2$ do not react with sulphur or selenium, and addition of an alkali acetate is also said to prevent oxidation.[43] Tellurium is attacked by concentrated aqueous chloric acid, and by chlorates at the end of the above list (magnesium, nickel, cobalt, zinc and cadmium).[43] Many sulphides and selenides react less readily than do sulphur or selenium, but there are some exceptions. Cupric sulphide explodes in contact with a concentrated solution of chloric acid or the chlorates of magnesium, zinc or cadmium; while antimonous, arsenious, stannous and stannic sulphides become incandescent in contact with these chlorates.[47] Moist chlorates explode in contact with white phosphorus, and inflame after a few moments with red phosphorus. Oxidation is vigorous with powdered arsenic, but is not appreciable with antimony or bismuth.[47] Mixtures of metal chlorates with some non-metals are, of course, employed in the preparation of well-known explosive and pyrotechnic compositions, and mixtures with hydrocarbons have been used.[48,49]

Sulphites are oxidized to sulphates by chlorates, but the rate of reaction is influenced considerably by the hydrogen ion concentration of the solution.[50-52] Oxidation is not detectable over a period of seven hours in a solution containing sodium sulphite and potassium chlorate, each in 0·1 N. concentration at 15° and containing 0·025 N-hydrochloric acid. In 0·05 N-acid, reaction occurs after an induction period of 20–40 minutes; the induction period increases if the concentration of sodium sulphite is increased. At acid concentrations above 0·075 N. the reaction proceeds smoothly without an induction period, and further increase in acidity has only a slight effect on oxidation rate. The induction period has been interpreted as resulting from accumulation of hydrogen ions by the reaction:-

$$ClO_3^- + 3HSO_3^- \rightarrow Cl^- + 3SO_4^{--} + 3H^+;$$

in support of this it is found that if the solution is buffered the oxidation rates are greatly modified.[51] Since potassium chlorate of high purity can be obtained, its use has been proposed in standardizing alkaline solutions; a solution of the chlorate of known concentration is boiled, and sulphur dioxide passed in for 30 minutes. A corresponding amount of sulphuric acid is formed:-

$$3SO_2 + KClO_3 + 3H_2O \rightarrow 3H_2SO_4 + KCl,$$

and this is titrated with the alkali.[47]

The oxidation of arsenites by chlorates requires a high acid concentration. Using hydrochloric acid, at least 2 N.solutions are required (preferably at 75°), and in the presence of sufficient acid there appears to be autocatalysis.[51,53] Sulphuric acid may also be used,[54] in spite of a statement to the contrary.[55] The reaction velocity depends more on the chlorate than the arsenite concentration, and the kinetic equation is:-

$$-d[ClO_3^-]/dt = k_1[ClO_3^-][AsO_3^{3-}] + k_2[ClO_3^-][Cl^-].$$

Osmium tetroxide catalyzes the reaction, and in its presence oxidation can be carried out, at 20°, in solutions of acidity as low as 0·05 N.[53] Electrometric measurements show that catalysis occurs through the formation of unstable addition compounds between reduction products of the osmium tetroxide and the chlorate.[56] Chlorates may be determined volumetrically, and in the presence of perchlorates, by adding an excess of a standard arsenite solution to an acidified solution of the chlorate, catalyzing the oxidation with a few drops of osmium tetroxide, and titrating the excess arsenite in the neutralized solution with iodine.[56] The same determination can be carried out by adding the chlorate solution to the arsenite dissolved in 5 N-hydrochloric acid, and containing iodine monochloride as catalyst. In this case the end point is detected potentiometrically.[57] As oxidizing agents for organic compounds, chlorates are activated by vanadium pentoxide, hydrogen peroxide, and potassium permanganate.[58]

In the oxidation of iodine to iodate by potassium chlorate, a little nitric acid is usually added to increase the rate of reaction. Reaction is more rapid in the presence of sulphuric or hydrochloric acid; the latter is most efficient because of the chlorine liberated ($HClO_3 + 5HCl \rightarrow 3Cl_2 + 3H_2O$), and the acid may in fact be replaced by a stream of chlorine. The chlorine forms iodine monochloride which reacts more rapidly with chlorate than does iodine itself, and in water gives some hypochlorous acid which also accelerates oxidation.[59] The oxidation of potassium iodide to iodine in aqueous solution has a temperature coefficient of 2·87 for the 25–35° interval; the reaction is catalyzed by vanadyl salts, but retarded by manganese sulphate and nickel sulphate.[60] When potassium iodide and potassium chlorate are fused together, some conversion to iodate occurs. The best yield of iodate is obtained with excess of potassium iodide, the yields for $KClO_3 : KI$ ratios of 1 : 1 and 1 : 2 being 42% and 62% respectively.[61] Chlorates oxidize bromides to bromine and ultimately to bromates. The kinetics of this process have been investigated; the reaction is catalyzed by arsenic acid, but not by arsenious acid or the arsenate ion.[62,63]

Oxidation of nitrous acid by chlorates takes place according to the equation:-

$$ClO_3^- + 3HNO_2 \rightarrow 3NO_3^- + Cl^- + 3H^+.$$

Reaction does not occur in neutral or alkaline solution, but commences immediately on acidification, so that it is probably the nitrous acid molecule rather than the nitrite ion which undergoes oxidation.[64,65] The reaction is of second order, and variation in chloride ion concentration produces no significant change in velocity constant.[66] In view of the strong reducing properties of hypophosphorous acid, it is surprising that it has so little action on chlorates. That no reaction occurs between dilute solutions has been confirmed, but slow reaction has been observed between concentrated solutions. For example, when chlorate solutions at least 0·25 molar are treated with 4 molar hypophosphorous acid, the chlorate is reduced in 36–48 hours.[67]

Chlorates oxidize thallous to thallic salts in concentrated hydrochloric acid solution, and the reaction may be employed in solution for the determination of thallous chloride, using iodine monochloride as catalyst and potentiometric detection of the end point.[57] Chromium is oxidized from the 3- to the 6-valent state. The reaction:-

$$Cr_2O_3 + MClO_3 \rightarrow 2CrO_3 + MCl,$$

proceeds quantitatively if the moist reactants are heated together in a sealed tube with calcium carbonate. If chromic oxide is boiled with an aqueous solution of an alkali chlorate, the amounts of oxide dissolved and chloride produced are again in 1 : 1 mol. ratio.[68] A perfectly dry mixture of anhydrous ferrous sulphate and potassium chlorate can be heated to 100° without reaction. In the presence of small quantities of water, chlorine dioxide and chlorine in approximately equal quantities are evolved, and in the presence of large amounts of water the chlorate is reduced quantitatively to chloride.[69] Reduction by ferrous sulphate is commonly used in the analysis of chlorates;[70-72] reduction in neutral solution is not entirely satisfactory, and slightly acid solutions are preferable. The kinetics of the reaction at 20° have been investigated. In the absence of a catalyst, the rate of reaction in high and constant concentrations of sulphuric acid is given by $-d[ClO_3^-]/dt = k[ClO_3^-][Fe^{2+}]$, and is proportional to the concentration of acid. The temperature coefficient is 2·73 for the temperature change 20° to 30°, and the activation energy 17675 g.-cal. In the presence of osmium tetroxide, which acts as a catalyst, the rate expression is more complex and the temperature coefficient and the activation energy are lower.[73]

The reaction between ammonia and potassium chlorate, which evolves much heat and can become explosive, has been studied by passing ammonia diluted with air over potassium chlorate absorbed in porous plate fragments placed in a combustion tube. The temperature at which reaction commences depends upon the ammonia concentration, but is below 300°. The reactions are:-

$$2KClO_3 + 4NH_3 \rightarrow 2KCl + 2N_2 + 6H_2O,$$

$$\text{and } 6KClO_3 + 4NH_3 \rightarrow 2KCl + 4KNO_3 + 2Cl_2 + 6H_2O.$$

About 60% of the nitrogen is converted into nitrate.[74] The reaction of potassium chlorate with ammonium salts is violent and complicated; with ammonium chloride, for instance, potassium chloride, potassium nitrate, hydrochloric acid, nitric acid, nitrous acid, oxygen, nitrogen and water have been identified in the reaction products.[75]

Some free metals reduce chlorates to chlorides. Potassium chlorate is reduced by metallic sodium at 100°;[76] the reaction products are sodium and potassium monoxides (with some peroxide), chlorine monoxide and chlorine dioxide.[77] Sodium hydroxide prepared electrolytically usually contains a little sodium chlorate, which is objectionable because of its corrosive properties. It may be reduced by adding finely divided metallic iron, which is oxidized to the oxide Fe_3O_4, at temperatures above 70°.[78,79] A metallic couple is more efficient, and chlorate may be removed quite rapidly by passing the solution through a bed of copper and iron turnings.[80] Reduction of chlorates by zinc, in acetic acid solution, is a well-known method employed in volumetric analysis; the use of Wood's metal in sulphuric acid at 90° is also satisfactory.[81]

On exposing neutral potassium chlorate solutions to ultra-violet light, decomposition occurs with evolution of oxygen.[82] In the light of a mercury arc (1900–2600 A.), the main decomposition reaction leads to the formation of hypochlorite and molecular oxygen:-

$$ClO_3^-,H_2O \rightarrow ClO^- + H_2O + O_2,$$

and the primary process of light absorption is believed to involve the transfer of an electron to the hydration layer. Irradiation of the hypochlorite causes decomposition to chloride:-

$$XO^-,H_2O \rightarrow X^- + H_2O + O,$$

and the oxygen so produced is responsible for some re-formation of chlorate.[83] The cathodic reduction of the chlorate ion is a well-known concomitant of its electrolytic preparation. The reduction efficiency is found to decrease with increasing cathode potential, and to be negligible for potentials greater than 1·5 V.[84] During electrolysis by silent electric discharge or glow discharge, chloric acid and its alkali salts are reduced at the anode as well as at the cathode. Decomposition into hydrochloric acid (or chloride) and oxygen is caused by energy-rich water molecules.[85,86] The reaction between hydrogen and solid chlorates in the silent electric discharge has also been investigated; lithium, sodium and calcium chlorates give the corresponding chlorides and water.[87,88] When submitted to the glow discharge from a Tesla coil in a vacuum, potassium chlorate decomposes to hypochlorite and chloride, and no chlorite or perchlorate is formed.[89,90] Attempts to oxidize potassium chlorate to perchlorate under oxygen pressures as high as 1200 atm. and at temperatures up to 475° were unsuccessful.[91] This is of interest in view of the failure to oxidize chloride to chlorate under similar conditions, which has already been mentioned (see page 583).

The Chlorates.

The discussion which follows deals with the physical, and some chemical, properties of individual salts: much of the recent work is concerned with sodium and potassium chlorates, with relatively few studies on other chlorates.

The very high solubility of lithium chlorate in water makes it possible to study the phase relations over almost the whole of the mol. fraction range. The phase diagram is shown in Fig. 2. Two hydrates, $LiClO_3,3H_2O$, (congruent m.p. 8°), and $LiClO_3,H_2O$, are formed. It is considered that the sections α, β and γ correspond with three solid forms of the anhydrous salt, and that the break in the curve at 21° represents a transition from the monohydrate to the anhydrous salt.[92] There is evidence, however, to suggest that the γ section of the curve corresponds with a hydrate $3LiClO_3,H_2O$, and that only two modifications of the anhydrous salt exist.[93-96] The solubilities and the solubility products of the alkali metal chlorates decrease rapidly with increase in atomic weight[97] (Table XVIII).

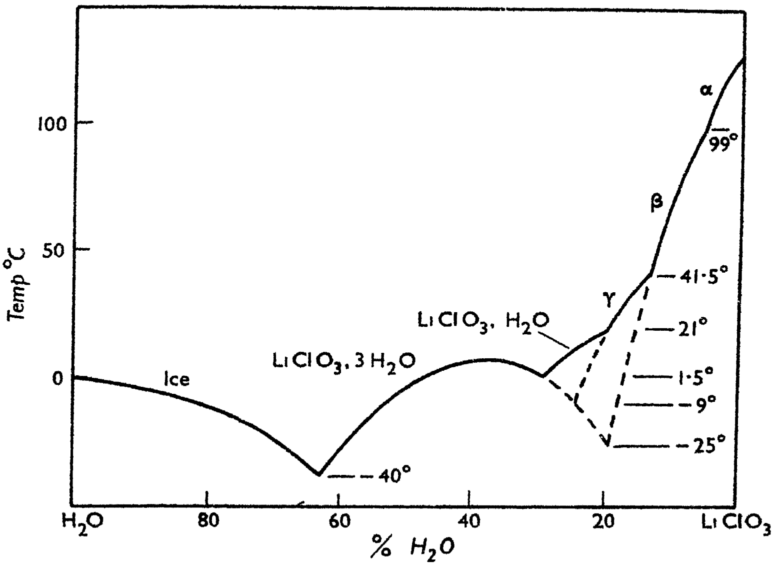

Fig. 2. LITHIUM CHLORATE-WATER PHASE DIAGRAM

TABLE XVIII.- SOLUBILITY AND SOLUBILITY PRODUCTS OF SOME METAL CHLORATES

Salt	Solubility (mols. salt/1000 g. H_2O)	Solubility Product
$LiClO_3$	18·32	336
$NaClO_3$	9·20	84·6
$KClO_3$	0·58	0·336
$RbClO_3$	0·32	0·102
$CsClO_3$	0·29	0·0841
$TlClO_3$	0·137	0·0188

The values for the solubility of sodium and potassium chlorates over a temperature range have been revised (Table XIX).

TABLE XIX. - INFLUENCE OF TEMPERATURE ON THE SOLUBILITY OF SODIUM AND POTASSIUM CHLORATES IN WATER

Temp. °C.	Solubility (g. salt/100g. saturated soln.)		Density of saturated $KClO_3$ solution
	$NaClO_3$[98]	$KClO_3$[99,100]	
0	44·32	3·2	1·021
10	46·70	4·9	-
20	48·95	6·8	1·042
30	51·30	9·2	-
40	53·54	12·2	1·073
60	-	19·2	1·115
100	67·10	36·0	1·219

The considerable difference between the solubilities of sodium and potassium chlorates is maintained in other solvents[101] (Table XX).

TABLE XX. - SOLUBILITY OF SODIUM AND POTASSIUM CHLORATES IN VARIOUS SOLVENTS AT 25°

Solubilities expressed as g. salt/100 g. solvent

Salt	Ethylene-diamine	Liquid ammonia	Mono-ethanolamine	Ethylene glycol	Water
$NaClO_3$	52·8	-	19·7	16·0	106
$KClO_3$	0·145	2·52	0·30	1·21	8·6

Potassium chlorate is slightly soluble (less than 0·01%) in liquid sulphur dioxide,[102,103] and its solubility in water-acetone,[104] and water-glycerol mixtures,[105] has been measured. The solubility of chlorates in deuterium oxide is appreciably less than in water;[106,107] and some comparative values are given in Table XXI.

TABLE XXI. - SOLUBILITIES OF CHLORATES IN WATER-DEUTERIUM OXIDE MIXTURES[107]

Salt	Temp.°	% D_2O	*Solubility in H_2O-D_2O	*Solubility in water	% difference
Potassium chlorate	5·0	91·43	0·5182	0·5845	12·4
Silver chlorate	5·0	98·38	0·6532	0·8017	18·8
Silver chlorate	15	98·38	0·9567	1·1481	17·0
Silver chlorate	25	98·38	1·3578	1·6040	15·6
Silver chlorate	35	98·18	1·9076	2·2353	14·9

* Solubilities are expressed as mols. salt/100 mols. (H_2O + D_2O)

Since chlorates and chlorides are frequently produced together and separated by fractional crystallization, the variation in chlorate solubility in the presence of chloride has important practical significance. This variation in the case of sodium salts is illustrated in Table XXII; the chlorate solubility is decreased by sodium chloride to a greater extent at high than at low temperatures.

The solubility of potassium chlorate in aqueous solutions of sodium chloride, of sodium carbonate and of potassium carbonate has also been recorded.[109]

TABLE XXII. - INFLUENCE OF SODIUM CHLORIDE ON SOLUBILITY OF SODIUM CHLORATE[108]

Temp. °C.	Solubility (g. $NaClO_3$/100 c.c. sat. soln.)			
	in water	in 10% NaCl	in 20% NaCl	in 30% NaCl
20	72·2	66	57·4	41·8
40	82·0	75	65	42
60	91·3	83·5	70	42·4
80	100·2	92	77	43·3
100	111·0	102	87	44

The osmotic and the activity coefficients of sodium and potassium chlorates have been determined;[110-112] some accurate values are given in Table XXIII.

TABLE XXIII. OSMOTIC AND ACTIVITY COEFFICIENTS OF SODIUM AND POTASSIUM CHLORATES AT 25°[110]

Sodium chlorate			Potassium chlorate		
Molar Concn.	Osmotic Coeff.	Activity Coeff.	Molar Concn.	Osmotic Coeff.	Activity Coeff.
0·1	0·927	0·772	0·1	0·913	0·749
0·3	0·904	0·688	0·2	0·887	0·681
0·5	0·892	0·645	0·3	0·867	0·635
0·7	0·885	0·617	0·4	0·849	0·599
1·0	0·880	0·589	0·5	0·832	0·568
1·6	0·874	0·553	0·6	0·816	0·541
2·0	0·876	0·538	0·7	0·802	0·518
2·5	0·879	0·525			
3·0	0·881	0·515			
3·5	0·886	0·508			

The heats of dilution of sodium chlorate are the same as for sodium bromate at concentrations below 0·0025 M., in agreement with their respective activity coefficients.[113] Some thermal properties of sodium chlorate solutions are collected in Table XXIV.

TABLE XXIV. - THERMAL PROPERTIES OF SODIUM CHLORATE SOLUTIONS[114]

(Concentrations expressed as mols. $NaClO_3$ per 100 mols. H_2O)

Integral Heat of Solution:	-3·51 kg.-cal./mol. (at saturation) -5·29 kg.-cal./mol. (at infinite dilution)
Differential Heat of Dilution:	-101 g.-cal./mol. (at saturation)
Specific Heat:	0·650 (concentration 15·39)
Partial Molar Heat:	-5 g.-cal./mol./degree (concn. 0·1) 35 g.-cal./mol./degree (concn. 15·0)
Partial Molar Volume:	3 c.c./mol. (concn. 0·25) 43 c.c./mol. (concn. 16)

The heat of solution of rubidium chlorate at infinite dilution and 25° is 11·41 kg.-cal./mol.[115] The endothermic nature of both heats of solution and of dilution indicates weak hydration of the chlorate ions.

Other physical properties studied include the depression of the freezing point of water by dissolved chlorates of lithium, sodium, potassium, rubidium and caesium,[116-119] the dielectric constant of dilute aqueous solutions of sodium and potassium chlorates,[120] the coefficient for absorption of ultrasonic waves by sodium chlorate solutions,[121] the magnetic birefringence of aqueous chlorate solutions,[122] the electrical conductivity of potassium chlorate solutions over the range 0 – 100°,[123] and the influence of the concentration of potassium chlorate on the compressibility of its aqueous solutions.[124] The fluidity of dilute solutions of potassium chlorate at 18° is represented by the equation:-[125]

$$\phi = 1 - 0{\cdot}0028c^{1/2} + 0{\cdot}049c - 0{\cdot}0275c^2,$$

where c is the molar concentration; the viscosities of the solutions, even at high dilution, are greater than that of pure water.[126] Using the more soluble sodium chlorate, the viscosities of supersaturated solutions have been measured. The viscosity-temperature graphs are smooth curves which show no irregularity at the saturation temperature.[127] Accurate determinations of the densities of dilute solutions of potassium chlorate are available, together with measurements of the change in volume which occurs during solution of the salt.[128,129] The calculated value for the contraction occurring on solution of one gram molecule of potassium chlorate at infinite dilution at 18° is 8·1 c.c.[128] In common with many other inorganic salts, chlorates increase the surface tension of water; the oscillating jet technique has been applied to these measurements.[130] In very dilute solution, the tension is slightly decreased, so that the tension values pass through a minimum.[131]

Sodium and potassium chlorates in the solid state have been studied extensively. Sodium chlorate forms cubic crystals, the unit cell containing four molecules, with a 6·570 ± 0·006 A.,[132] or 6·559 A.[148] These determinations follow much preliminary work with which they are in general agreement.[133-143] Sodium chlorate is a suitable substance for observations on crystal growth.[144,145] The cubic habit is generally unresponsive to modification, but the presence of certain ions in the solution from which its crystals are grown (especially the type RO_4^{2-}, e.g. SeO_4^{2-}, CrO_4^{2-}) can cause 111 planes to appear at the expense of 100 planes.[146,147] Mixtures of sodium chlorate and sodium bromate give a series of cubic crystals which are completely isomorphous, the cell size increasing to a = 6·719 A. for pure sodium bromate.[148] With potassium chlorate, with which sodium chlorate is not isomorphous, no solid solution is formed,[148] though there is one report to the contrary.[149] Potassium chlorate and potassium bromate do not form solid solutions.[148] The diffuse scattering of *X*-rays by sodium chlorate crystals has been investigated, but there is as yet no agreed interpretation of the observations.[150-152] The spatial distribution of atomic displacements in sodium chlorate crystals owing to thermal vibration may be calculated from the elastic constants[152,153] and compressibility.[155] Values for the various constants are given in Table XXV.[154]

TABLE XXV. - ELASTIC (AND RELATED) CONSTANTS FOR SODIUM CHLORATE CRYSTALS

Elastic constant C (× 10^{11} dynes /cm²)			Elastic moduli s (× 10^{-13} cm²/dyne)			Compressibility (× 10^{-13} cm²/dyne)
C_{11}	C_{12}	C_{44}	s_{11}	s_{12}	s_{44}	
4·9	1·38	1·17	23·35	–5·15	85·4	39·1
4·9	1·45	1·19	23·5	–5·30	84·1	38·7

The elastic constants are smaller, and the compressibilities larger, than the corresponding values for sodium bromate.[154] The coefficient of linear expansion of solid sodium chlorate is 44·92 × 10^{-6} at 34·2°C., increasing to 59·50 × 10^{-6} at 225·9°. The fact that these values exceed those for sodium bromate is consistent with the higher melting point and smaller interatomic distances in the latter.[156] The free energy of formation of sodium chlorate is –59·1 kg.-cal./mol., and the entropy, S_{298}, is 30·2 ± 1·0 g.-cal./degree/mol.

(compared with $KClO_3$ = 34·17, $AgClO_3$ = 35·8, $TlClO_3$ = 40·4).[157] Measured by the liquid mixture method, the dielectric constant of crystalline sodium chlorate is 5·9.[158]

Crystals of potassium chlorate were shown, by use of the ionization spectrometer, to be monoclinic.[159] *X*-Ray analysis confirmed that the crystals were monoclinic holohedral, of space group C^2_{2h}. The unit cell contains two molecules, and has dimensions a = 4·647, b = 5·585, and c = 7·085 A., β = 109°38′.[160,161] The refractive indices are 1·4099, 1·5174 and 1·5241.[162,163] The structure bears a marked similarity to that of calcite, which no doubt explains the analogous optical properties, cleavage and twinning which the two substances display.[164] It has been confirmed that the iridescence which can occur in potassium chlorate crystals is due to reflection of light by twinned crystal planes.[165-167] The growth of potassium chlorate crystals, and the variation of crystal habit in the presence of ionic impurities, has been studied, and it has been shown that added ions of the type RO_4^{2-} have a pronounced influence on crystal habit;[168-170] in the presence of potassium manganate, extremely thin crystals of the order of 600 A. in thickness (90 unit cells) can be obtained.[170] The density of solid potassium chlorate at 20° is 2·3383 and 2·3385, determined by the suspension and pyknometer methods respectively.[171] Some measurements of the refractive index of molten sodium and potassium chlorates have been made.[172]

In the reciprocal salt pair, $NaCl + KClO_3 \rightleftharpoons NaClO_3 + KCl$, the left hand pair is stable, and represents the couplet whose salts have the lowest solubility product and exist as excess salt in the presence of water. This has been observed by measurements at 20°,[173] and in the 0 – 40° range, and this salt pair is probably stable up to 100°. Isothermally invariant points for the system in water have been determined.[174] In the salt pair, $2NaCl + Ba(ClO_3)_2 \rightleftharpoons 2NaClO_3 + BaCl_2$, the compounds on the left again represent the couple stable at 20°.[175] In the system $NaClO_3$–Na_2SO_4–H_2O, the solid phases at 0° and 20° are the compounds $Na_2SO_4,10H_2O$ and $NaClO_3$; at 40° the two anhydrous salts form the solid phases.[176] At temperatures above 25°, there is evidence for a double salt $NaClO_3,3Na_2SO_4$ which has a narrow range of stable existence but can persist in metastable equilibrium over a wide concentration range.[177] There is no evidence of double salt formation in the corresponding system $KClO_3$–K_2SO_4–H_2O,[177] or in the systems $NaCl$–$NaClO_3$–H_2O,[178] $2NaClO_3 + K_2CO_3 \rightleftharpoons Na_2CO_3 + 2KClO_3$,[179] $2KClO_3 + CaCl_2 \rightleftharpoons 2KCl + Ca(ClO_3)_2$,[180] $KClO_3$–KBr–H_2O,[181] and $KClO_3$–KI–H_2O.[181] The equilibria in the system $KClO_3$–KNO_3–H_2O provide some evidence for double salt formation.[182]

The preparation of ammonium chlorate, and its explosive properties, have already been fully described (Mellor,II,338-9) but further information on the stability of its aqueous solutions is now available.[183] On keeping for long periods the cold saturated solution undergoes no apparent decomposition, but in the presence of a solid phase some decomposition is evident within a few days, and may become violent if much solid phase is present. Decomposition is autocatalytic if the reaction products are not removed from the system. The ammonia is oxidized to nitrogen and nitric acid; the latter can react with chlorate to give chlorine dioxide and chloric acid, which are stronger oxidizing agents. No perchlorate is formed in the reaction, and the solid residue consists of ammonium nitrate with no chloride.[183]

Under suitable conditions, chlorination of magnesium hydroxide suspensions gives a basic magnesium chlorate, $Mg(ClO_3)_2,4Mg(OH)_2$, which is stable in concentrated solution from 25° to 125°. *X*-Ray powder data show that it is isomorphous with the basic nitrate, $Mg(NO_3)_2,4Mg(OH)_2$.[184] Thermal analysis of the calcium chlorate–water system shows the existence of a series of hydrates. The hydrates separate in the following order: at −41°, $Ca(ClO_3)_2,6H_2O$; at −27°, $Ca(ClO_3)_2,4H_2O$; at −8°, $Ca(ClO_3)_2,2H_2O$; and at 76° the solid

Refs. p. 592

phase is the anhydrous salt.[185] The cryoscopy of several electrolytes in the molten hexahydrate has been studied,[186] as also has been the cryoscopy of beryllium, magnesium, calcium, strontium and barium chlorates in aqueous solutions.[187] In the system, $Ba(ClO_3)_2$-$Ba(BrO_3)_2$-H_2O, the monohydrates of the two salts form a continuous solid solution at 25°, so that chlorate-bromate mixtures cannot be separated satisfactorily in analysis by precipitation with excess of a barium salt.[188] Crystals of strontium chlorate, in common with many other chlorates, show piezoelectric properties.[189]

Gallium chlorate has been prepared by metathesis from gallium sulphate and barium chlorate.[190] The chlorates of several hydroxy- or acetato- lead complex cations have been isolated. They are given the formulae $[Pb_2(OH)_2](ClO_3)_2,H_2O$, $[Pb_3(OH)_4](ClO_3)_2$, $[Pb_2(OH)(Ac)](ClO_3)_2,2\frac{1}{2}H_2O$ and $[Pb_3(OH)_2(Ac)_2](ClO_3)_2,3H_2O$,[191] but it is not certain that the cation complexes really have the structure shown. The chlorates of metal-ammine complexes of copper, cadmium, nickel, cobalt and zinc are prepared by treating the cold, stirred solution of the metal chlorate with ammonia gas. The ammine salts are precipitated, and may be filtered off and dried. The compounds are highly explosive, and detonate when struck. Tetramminocupric chlorate is capable of initiating the explosion of trinitrotoluene. The nitrogen produced results from intramolecular oxidation-reduction, the ammonia being oxidized at the expense of the chlorate group. The compounds are highly deliquescent, and lose ammonia in moist air. Corresponding hydrazine compounds may be prepared by treating the cold stirred solution of the metal chlorate with hydrazine hydrate dissolved in water or alcohol. The precipitates are washed and dried at a low temperature. The compound $[Ni(N_2H_4)_3](ClO_3)_2$ corresponds to the hexammine. These hydrazine compounds are also explosive, the copper compound detonating on drying at room temperature. The perchlorates of both types of compound are also explosive, but are less sensitive than the chlorates.[192]

Silver chlorate is obtained by adding 170 g. of silver nitrate in 100 ml. of water to 106 g. of sodium chlorate in 100 ml. of water, each at 85°. On cooling to 0°, decanting, and washing with 50 ml. of water at 0°, a 78% yield of 95% pure silver chlorate is obtained. The purity is increased to 99·7% by two recrystallizations from 125 ml. of water.[193] Silver chlorate gives tetragonal crystals, but the crystals are not holohedral and have no observed piezoelectric porperties. The unit cell contains 8 molecules, with dimensions $a = 8{\cdot}48$, $c = 7{\cdot}91$ A. The crystals have a density of 4·37, and are isomorphous with silver bromate.[194-196] In aqueous solution, the equivalent conductivity of silver chlorate at infinite dilution is 126·57.[197]

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PERCHLORIC ACID AND THE PERCHLORATES

Preparation.

The references to preparation of perchlorates by the action of heat on chlorates are few in number compared with those concerned with electrolytic oxidation. The presence of impurities in the chlorate, such as free metals and metal oxides, leads to decomposition into chloride and oxygen rather than into perchlorate and chloride. Iron vessels cannot therefore be used, and quartz vessels have been recommended as giving the highest yield of perchlorate.[1,2] Even the alkali in glass is sufficient to lower the yield. The optimum temperature at which to hold the melt is 470 – 550° for potassium perchlorate, and a little lower for sodium perchlorate.[1,3,4] Potassium perchlorate is obtained in poor yield when the chlorate is treated, under appropriate conditions, with one of the reagents – sulphuric acid, concentrated or anhydrous nitric acid, phosphoric acid or chromium trioxide – although many oxidizing agents are without effect on potassium chlorate.[6] Contrary to an earlier observation,[5] silver oxide does not oxidize a chlorate to perchlorate; it is decomposed before an appreciable amount of potassium perchlorate is formed, and the lower yields of perchlorate are no doubt due to its catalyzing the decomposition into chloride and oxygen.[2,3] Perchloric acid solutions of high concentration are obtained by treating anhydrous sodium or barium perchlorate with a little more than the equivalent amount of concentrated hydrochloric acid. The precipitated chloride is filtered, and the filtrate concentrated by vacuum distillation.[7,10] The anhydrous acid may be obtained from the aqueous solution by distillation under reduced pressure, but the process is more efficient if sulphuric or phosphoric acid is added. Details of suitable distillation plant have been described.[8,9]

Conditions under which the chlorate ion undergoes anodic oxidation to the perchlorate ion can be readily achieved, and this electrolytic oxidation is the more important process in perchlorate preparation. The principles involved have been discussed (Mellor,II,374–375). The chlorate concentrations employed vary widely; with a current density of 3 amp./cm^2, a solution containing only 0·6 g./litre of sodium chlorate may be used,[11] whilst the electrolysis of solutions containing 800 g./litre, in which the solution is maintained at a concentration just below saturation, has also been described.[12] Anodes of platinum,[20,21] lead dioxide or stainless steel, or an anode plated with chromium, have been used, and the efficiency of anodic oxidation is increased by as much as 30% if sodium fluoride is added to the solution.[13] As with chlorate production, the addition of a chromate to the solution minimizes cathodic reduction.[14] The yield of perchlorate is reduced in the presence of chloride, since the latter also undergoes anodic oxidation.[15-17] It is not true however, as was at one time supposed, that oxidation of chlorate to perchlorate does not take place until all chloride is oxidized; provided that high current densities (2 amp./cm^2) are used, small amounts of sodium perchlorate are formed during electrolysis of sodium chlorate solutions in the presence of 18% of sodium chloride.[16] Potassium chlorate solutions may be electrolyzed at 27° and at a current density of 0·15 amp./cm^2 to produce potassium perchlorate,[18] but the low solubility of the potassium compared with the sodium salts restricts the range of experimental conditions available. It is usually prepared by metathesis from sodium perchlorate and potassium chloride, when potassium perchlorate separates from solution.[19-21]

Since chlorates are themselves produced by anodic oxidation from chlorides, perchlorate may be prepared by the electrolysis of aqueous solutions of metal chlorides.[15,22-24] Using the alkali metal chlorides, lithium chloride gives the highest yields of perchlorate. With the alkaline earth metal chlorides, oxidation is most efficient in the case of calcium chloride; the initial pH of the solution has little influence, but the efficiency is somewhat lower in alkaline solution. Increase in temperature (from 25° to 65°) has the same effect, and cannot be compensated by increase in concentration. The influence of the cation on the efficiency of electrolytic preparation is illustrated in Table XXVI.

TABLE XXVI. - ELECTROLYTIC PREPARATION OF PERCHLORATES[15]

Salt Electrolyzed	Perchlorate yield (g. equiv. × 10^3/amp.hour)	Current Efficiency %
LiCl	4·1	94·4
NaCl	1·05	43·9
KCl	1·1	47·3
$MgCl_2$	1·95	36·8
$CaCl_2$	4·7	89·3
$BaCl_2$	2·2	54·7

(Experimental conditions: platinum electrodes without diaphragm; concentration 3·5 N.; current density 0·5 amp./sq.dm.; temperature 25°).

With the alkali metal chlorides, the relative proportions of chloride, chlorate and perchlorate present in the solution during electrolysis are influenced considerably by the size of the cation (Table XXVII).

TABLE XXVII. - ANODIC OXIDATION OF ALKALI METAL CHLORIDES[15]

Salt Electrolyzed	Time before first appearance of perchlorate (min.)	Composition of salt after passage of 150 amp.hours		
		Chloride	Chlorate	Perchlorate
LiCl	90	0·96	15·25	83·79
NaCl	162	15·5	37·7	46·8
KCl	200	16·2	43·7	40·1
RbCl	-	0·8	99·2	0·0

(Experimental Conditions: as in Table XXVI, but temp. = 60°C.)

In the electrolysis of rubidium chloride solution, anodic oxidation proceeds only as far as rubidium chlorate. Having a low solubility, this salt separates out and cannot be further oxidized.[15] In place of platinum, lead dioxide or silicon carbide has been used for the anode.[25,26] As an alternative te chloride as a starting material, a hypochlorite may obviously be used, and the electrolytic preparation of sodium perchlorate from sodium hypochlorite has been carried out using a lead dioxide anode, with platinum, silver, gold or rhodium as the cathode.[27] Perchloric acid may be prepared directly by electrolysis of hydrochloric acid, and an apparatus consisting of sheet silver (which serves as cathode) with lead as anode has been described.[28]

PROPERTIES OF PERCHLORIC ACID

The anhydrous acid is a colourless, very mobile liquid, m.p. -112°. On vacuum distillation it breaks up to some extent into water and its anhydride, dichlorine heptoxide, and the distillate contains about 50% of this anhydride. On heating at atmospheric pressure, it undergoes more complete decomposition, often explosively, into oxygen, water and oxides of chlorine. On standing in the cold it decomposes slowly, and it is a violent oxidizing agent, especially towards organic compounds. The Raman spectrum of the anhydrous acid is different from that of the ClO_4^- ion, and contains some lines identical with those for the Cl_2O_7 molecule; it shows that the chlorine atom is surrounded by four oxygen atoms arranged tetrahedrally, with the hydrogen atom attached to one of them.[29-33] There is no molecular association in the liquid. An outstanding feature in perchloric acid chemistry is the readiness with which the covalent molecule will donate a proton to any group able to accept it, leaving the highly stable ClO_4^- ion. In this ion, the four oxygen atoms are bonded to the chlorine atom by identical co-ordinate links, and all the valency electrons of the chlorine atom are shared. The stability of the ion arises from the resistance which this symmetrical tetrahedral structure exhibits towards any bond formation which would result in its deformation. In consequence, it is probably the strongest acid known; pure nitric acid does not function as an acid (in the Brønsted sense) in solution in perchloric acid, but rather as a base, being transformed into the compound $(H_2NO_3)^+ClO_4^-$.[30] It is the only compound capable of functioning as an acid in solution in anhydrous hydrofluoric acid, in which the reaction, $HF + HClO_4 \rightarrow (H_2F)^+ClO_4^-$, occurs.[34] For the same reason, perchloric acid has the greatest influence of any acid in increasing the equilibrium constant of the reaction, $H_3PO_4 + HF \rightleftharpoons H_2PO_3F + H_2O$, since, by its readiness to form hydroxonium perchlorate, it shows the greatest affinity for water.[35] Perchloric acid is said to give normal values for the cryoscopic constant of pure sulphuric acid when dissolved in that liquid.[36]

The proton donating power of perchloric acid accounts for the remarkable stability of the monohydrate $HClO_4,H_2O$. The melting points of all other hydrates are below 0°, while the monohydrate melts at +50°C. (Determined with high accuracy, the m.p. is 49·905 ± 0·005°).[37] The formulation of this hydrate as hydroxonium perchlorate, $[H_3O]^+[ClO_4]^-$ has been confirmed by comparing its *X*-ray pattern with that of ammonium perchlorate, when the two were found to be practically identical,[38] and by the presence of a band characteristic of the ion $[H_3O]^+$ in the Raman spectrum of the monohydrate.[39] Its density is calculated to be 1·88.[38] On addition of water to perchloric acid in 1 : 1 molar amount, it would be anticipated that complete conversion to the monohydrate would occur, but Raman spectra measurements indicate that this is not entirely true. Lines characteristic of the ClO_4^- ion appear after the addition of 3% of water, but the $HClO_4$ lines persist at acid concentrations down to 75%,[32,33] or even 70%,[40] though the monohydrate contains 85% of perchloric acid. It is unlikely however that the undissociated acid is present in any appreciable concentration. Some relevant thermodynamic properties are given in Table XXVIII.

The formation of perchloric acid hydrates has an influence on a number of the physical properties of aqueous perchloric acid solutions. Measurements on the electrical conductivity of these solutions show that the specific conductivity passes through a maximum at 37% perchloric acid.[41-43] Accurate values are shown in Fig. 3.[43] Measurements carried out at 60° (*i.e.* above the m.p. of the monohydrate) show that on adding water to pure perchloric acid,

TABLE XXVIII. – THERMODYNAMIC PROPERTIES OF PERCHLORIC ACID AND ITS HYDRATES[59]

State	Heat of Formation $-\Delta H$ kg.-cal./mol.
Pure anhydrous liquid	11·1
Infinite dilution in water	31·41
$HClO_4,H_2O$ (crystalline)	92·1
$HClO_4,2H_2O$ (liquid)	162·8

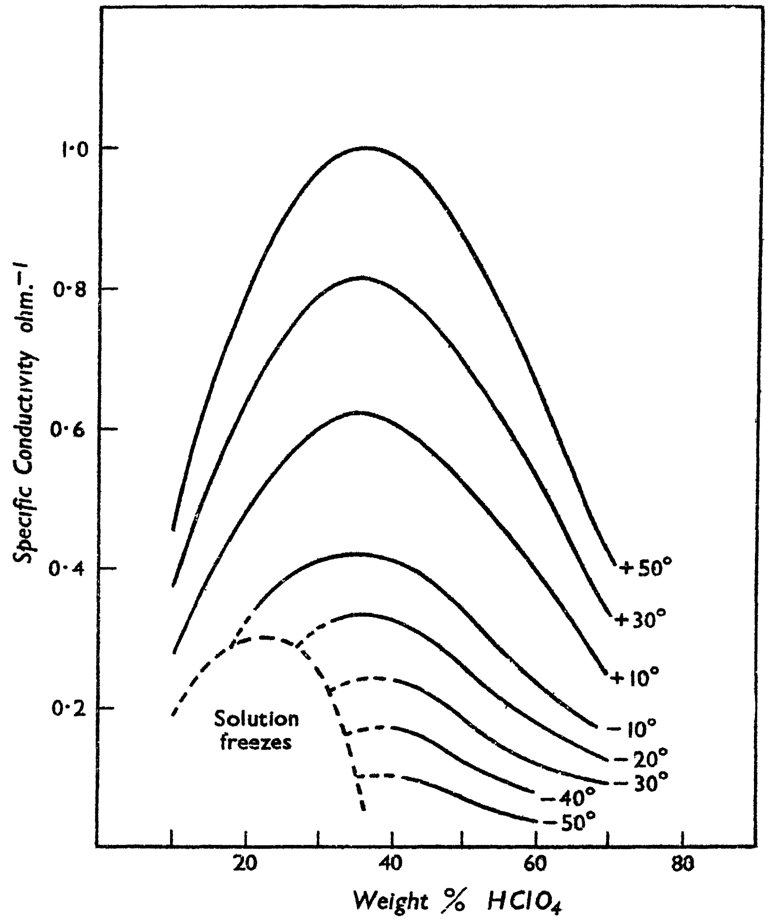

Fig. 3. SPECIFIC CONDUCTIVITY OF AQUEOUS PERCHLORIC ACID SOLUTIONS

the conductivity increases to a slight maximum at 54·3 mol.% acid, and then passes through a pronounced maximum as shown in Fig. 3.[48] When these values are corrected for changes in viscosity (by multiplying by the viscosity) the curves assume quite a different form, and there is a maximum at 33 mol.% $HClO_4$.[50] This, together with the corresponding viscosity data, indicates the presence of the monohydrate and the dihydrate in the liquid phase. The dissociation constant of perchloric acid in pyridine is $7{\cdot}55 \times 10^{-4}$.[44] In ethylene dichloride solution at 25° the ionic mobility of the perchlorate ion is 39·2,[45] compared with a value of 67·32 ± 0·06 in water at 25°.[46]

The resistivity and kinematic viscosity of aqueous perchloric acid solutions are related by the empirical equation:-

$$\frac{\log(20 \times \text{kinematic viscosity})}{\sqrt{T}\,.\,\log(4 \times \text{resistivity})} = K = 0{\cdot}1.$$

The value of K is remarkably constant over the 30%-60% concentration range.[43] The viscosities vary widely (by a factor up to 90) with change in concentration and temperature.[43,47] Values are given in Table XXIX.[43]

TABLE XXIX.- VISCOSITY OF PERCHLORIC ACID SOLUTIONS IN WATER

% $HClO_4$ by weight	Absolute viscosity (centipoises)				
	-50°	-20°	0°	20°	50°
10	-	-	1·714	1·010	0·569
20	-	-	1·707	1·043	0·610
30	-	3·415	1·815	1·139	0·684
40	18·21	3·928	2·113	1·345	0·822
50	90·9	5·732	2·914	1·821	1·099
60	-	9·962	4·713	2·813	1·646
70	-	14·19	7·333	4·504	2·639

The viscosities increase with acid concentration at all temperatures, but if measured over the full concentration range at temperatures above the m.p. of the monohydrate, the viscosity passes through a maximum at 42·5 mol.% (80·5 wt.%) of perchloric acid.[48] The composition of maximum viscosity in systems of perchloric acid with a second component does not always coincide with the stoicheiometric ratio in which the two form an addition compound because of interaction between the addition compound and the second component,[54] but the shape of the viscosity-composition curve gives a valuable guide to the extent of compound formation. When the viscosity changes regularly with composition, no addition compound is formed; an S-shaped curve indicates that one of the components is associated to a higher degree than is the compound, and a maximum in the curve indicates strong compound formation.[55] This is illustrated in an interesting series of measurements on systems formed by perchloric acid with acetic acid and its chlorine derivatives[56] (Table XXX).

TABLE XXX.- SYSTEMS FORMED BY PERCHLORIC ACID WITH THE CHLOROACETIC ACIDS

System: Perchloric acid with	Viscosity	Compounds formed	Reference
$CCl_3.COOH$	varies regularly	No compounds	53
$CHCl_2.COOH$	S-shaped	$HClO_4,CHCl_2.COOH$ $2HClO_4,CHCl_2.COOH$	52
$CH_2Cl.COOH$	shows maximum at 33 mol.% $HClO_4$	$HClO_4,CH_2Cl.COOH$	51
$CH_3.COOH$	maximum at 33 mol.% $HClO_4$	$HClO_4,CH_3.COOH$ $HClO_4,2CH_3.COOH$	49

The mixing of trichloroacetic acid and perchloric acid is accompanied by expansion in volume, whereas in the other systems in Table XXX (and including water)[57] a contraction occurs. The proton donating power of acetic acid is small compared with that of perchloric acid, and compound formation occurs by proton transfer. With increasing substitution by chlorine, the acidity of the acetic acid increases; compound formation is weak with dichloroacetic acid, and no acid-base interaction whatsoever occurs with trichloroacetic acid. The conductivity, viscosity and surface tension of perchloric acid-sulphuric acid mixtures have also been examined, and no evidence for interaction has been observed.[58]

The freezing point diagram for perchloric acid-water mixtures (Mellor,II, 378) from which data on the full range of hydrates were first obtained, has not been modified. A re-examination of the system over part of the concentration range is in general agreement.[43] The densities of the solutions are required in many physical studies and have been determined accurately.[43,60] Some values are given in Table XXXI.

TABLE XXXI. - DENSITIES OF PERCHLORIC ACID SOLUTIONS IN WATER[43]

% of $HClO_4$ by weight	Density (g./ml.)				
	-50°	-25°	0°	25°	50°
10	-	-	1·0637	1·0560	1·0437
20	-	-	1·1356	1·1228	1·1075
30	-	1·2312	1·2168	1·2002	1·1821
40	1·3515	1·3308	1·3111	1·2908	1·2703
50	-	1·4528	1·4255	1·3999	1·3752
60	1·6300	1·5908	1·5580	1·5275	1·4994
70	-	1·7306	1·6987	1·6644	1·6344

Both dynamic[61] and isopiestic[62] vapour pressure measurements have been carried out on aqueous perchloric acid solutions. Values are given in Table XXXII, together with values of $(p_0 - p)/p_0$ from which activity coefficients are calculated.

TABLE XXXII. - VAPOUR PRESSURE OF PERCHLORIC ACID SOLUTIONS IN WATER AT 25°C.[61]

Molal concentration of $HClO_4$	Vapour pressure p(mm.)	$\frac{p_0 - p}{p_0}$
0·0	23·752	-
0·20064	23·593	0·006694
0·60655	23·254	0·020967
1·01589	22·870	0·037134
3·1512	20·192	0·149882
5·4347	16·308	0·313405
7·8719	11·490	0·516251
10·5132	6·838	0·712108

There has been some discussion concerning the calculation of the activity coefficients of perchloric acid from vapour pressure data,[61,63,64] but the values given in Table XXXIII, together with the corresponding osmotic coefficients, are now considered to be correct.

For concentrations up to 0·6 molar, the activity coefficients are almost identical with those for hydrochloric acid. At higher concentrations the perchloric acid values are abnormal, and increase rapidly. This is attributed to the pronounced hydration effect in perchloric acid solutions.[61] The aqueous solution forms a constant boiling mixture (72·4% acid at 203°). This is a powerful dehydrating agent; it has also been proposed as a more

TABLE XXXIII.- MEAN ACTIVITY COEFFICIENTS[65] AND OSMOTIC COEFFICIENTS[62] OF PERCHLORIC ACID IN AQUEOUS SOLUTION AT 25°C.

Molar concentration m	Activity coefficient $f_{\pm}$	Osmotic coefficient f_0	m	$f_{\pm}$	f_0
0•2	0•766	0•951	5•0	2•94	1•860
0•4	0•754	0•966	6•0	4•41	2•106
0•6	0•763	0•988	7•0	6•90	-
0•8	0•784	1•013	8•0	11•32	-
1•0	0•810	1•041	9•0	18•0	-
2•0	1•039	1•210	10•0	29•0	-
3•0	1•420	1•406	11•0	47•3	-
4•0	2•018	1•622	12•0	77•7	-

convenient standard than constant boiling hydrochloric acid in acidimetry.[66,67]

Addition of perchloric acid to water causes an initial fall in surface tension, for which hydrogen-bond formation at the surface has been considered responsible. The tension passes through a minimum with increasing concentration. the position of the minimum varying with temperature, and then through a shallow maximum. The concentration at which the maximum occurs is independent of temperature, and corresponds to the composition $HClO_4,3H_2O$.[68] Values are given in Table XXXIV.

TABLE XXXIV.- SURFACE TENSION OF PERCHLORIC ACID SOLUTIONS IN WATER[68]

% $HClO_4$ by weight	Surface tension dynes/cm.		
	15°	25°	50°
0•00	73•51	71•98	68•16
10•01	71•66	70•34	66•97
30•36	69•82	68•57	65•66
40•37	69•72	68•49	65•74
60•70	70•88	69•69	67•40
63•47	70•77	69•73	67•44
67•59	70•67	69•71	67•41
72•25	69•96	69•01	66•85

The refractive indices at 25° (for the D_3 helium line, λ = 587 mμ) of aqueous solutions of perchloric acid containing 54•158, 64•855 and 69•522 wt.-% of acid are 1•38780, 1•40640 and 1•41400 respectively.[69] When the molar refractions are plotted against acid concentration, a smooth curve is obtained with a minimum at 18% acid.[69,70] Apparent molal volumes have also been calculated.[69-72] From refractive index and density data, the radius of the ClO_4^- ion is calculated to be 1•82 A.[73]

Because of the stability of the perchlorate ion, perchloric acid in aqueous solution is reduced only under extreme conditions. Electropositive metals (such as iron or zinc) are attacked by the solution, but with the formation of hydrogen and the metal perchlorate.[74] The oxidizing power of the acid is attributed to the undissociated acid rather than to the perchlorate ion. Chromous salts reduce the acid slowly;[76] the rate of oxidation of chromium salts depends on the concentration and temperature of the acid. Under pressure in a sealed tube, oxidation of a chromium salt begins at 130° with an 80% solution, at 170° with 65% acid, and at 260° with 20% acid.[75] Salts of trivalent titanium and molybdenum also reduce perchloric acid, and the kinetics of the reduction process in the presence of added hydrochloric and sulphuric acids have been studied. The velocity of reduction by titanous salts increases threefold with 10° rise in temperature. Rates of reduction by molybdenum salts depend upon the degree of complexity of the salt; under standard conditions the times required for reduction of the same amount of perchloric acid are: $Ti^{3+}:Cr^{2+}:Mo^{3+}$(olive green)$:Mo^{3+}$(orange) $= 1:1300:18:40000$.[76] Perchlorates are not reduced by ferrous sulphate or by sulphurous acid, but reduction by titanous chloride or sulphate is sufficiently rapid to be applicable in the quantitative determination of perchlorates.[90]

Hydrochloric acid is not a reducing agent, but hydrobromic acid reduces perchloric acid in solution at 100°. The reaction is catalyzed by tetravalent osmium compounds.[77] In a sealed tube, iodides are oxidized by perchloric acid to iodates. At 135° oxidation to iodine occurs, and at 200–210° the iodine colour disappears, the overall reaction being:-

$$7HClO_4 + 4KI = 4HIO_3 + 3HCl + 4KClO_4.$$

No free oxygen is liberated. Organic iodo-compounds are usually decomposed completely into water, carbon dioxide and iodic acid under these conditions.[78] The products of the reaction of 65% perchloric acid with a range of simple organic compounds (alcohols, acids, hydrocarbons) in a sealed tube at 135–220° were found to be invariably oxides of carbon and hydrogen chloride, with no free oxygen. This suggests that the oxidation is due to the direct action of perchloric acid, and not to its decomposition products.[79] When perchloric acid is used in the destruction of organic residues, explosions may sometimes occur,[80-83] but may be avoided by giving the residues an initial treatment with fuming nitric acid.[80-82,91]

Perchloric acid dissolves in a number of non-aqueous solvents. It is miscible with liquid hydrocyanic acid, with some heat evolution,[84] and its solution in nitric acid,[85,86] ethylene dichloride and pyridine has been mentioned above. With pyridine, perchloric acid forms a stable compound $C_5H_5N,HClO_4$, which will exist as pyridinium perchlorate, $C_5H_5NH^+.ClO_4^-$; it melts at 288°, decomposes at 335–340°, and may explode violently (probably by intramolecular oxidation-reduction) in contact with metals. The compound is employed in the preparation of pure pyridine. Serious explosions have occurred when the process has been used,[87,88] but it can be modified to preclude danger of explosion.[89]

Perchloric acid has many uses. A eutectic mixture of perchloric acid and water provides a suitable electrolyte, at temperatures below −50°, for the electrolytic preparation of ozone. A cell having a platinum anode and lead cathode has been described.[92] In the electrolytic preparation of peroxysulphuric acid, addition of perchloric acid improves the yield by increasing the overvoltage.[93] A solution of 40–60% acid is also used in the lead-perchloric acid primary cell.[94] The acid has been used for many years in the analysis of silicates,[95,96] and finds important application in steel analysis.[97] In these analyses also there is always some risk of explosion unless conditions are carefully controlled.[98,99] In organic chemistry, perchloric acid is used, like picric acid, to identify compounds by the formation of characteristic salts.[100]

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PROPERTIES OF THE PERCHLORATES

Several properties of the alkali perchlorates as a group may first be considered. The anhydrous salts are isomorphous with each other, and with thallium, silver and ammonium perchlorates, the alkaline earth sulphates, and potassium permanganate.[1-7] The crystal structures of the series have been determined by optical and *X*-ray methods,[2,3,5,6,8-11] some of the data being tabulated in Table XXXV.

Values differing from those in Table XXXV are quoted by other workers.[6] The perchlorate ion forms a regular tetrahedron,[6] though there is a statement that it forms an irregular tetrahedron in the ammonium and potassium salts.[9,10] Evidence of a different type suggests that only a model with rotating perchlorate groups can explain the high temperature behaviour of sodium perchlorate.[12] A transformation of the ordinary rhombic forms of the perchlorates,

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TABLE XXXV. - CRYSTAL STRUCTURES OF ALKALI METAL PERCHLORATES

Salt	Cell Dimensions			Space group	Reference
	a	*b*	*c*		
$LiClO_4,3H_2O$	7·71	-	5·42	C_{6v}^4	11
$NaClO_4$	6·48	7·06	7·08	V_h^{17}	6
$KClO_4$	8·834	5·650	7·240	V_h^{16}	10
$RbClO_4$	9·27	5·81	7·53	V_h^{16}	5
$CsClO_4$	9·82	6·00	7·79	V_h^{16}	5
NH_4ClO_4	9·202	5·816	7·449	V_h^{16}	10

with the exception of lithium, into a regular isotropic form has been observed.[16] The temperatures are: sodium 308°, potassium 299–300°, rubidium 279°, cæsium 219° and ammonium 240°.

The solubilities of the alkali perchlorates have been determined at 25° in water, ether, acetone, ethyl acetate and methyl, ethyl, *n*-propyl, *n*- and *iso*-butyl alcohols.[13] Representative values are given in Table XXXVI.

TABLE XXXVI. - SOLUBILITIES OF PERCHLORATES AT 25°
(g./100 c.c.SOLN.)

Salt	Water	MeOH	*n*-BuOH	$COMe_2$	AcOEt
$LiClO_4$	47·42	89·44	49·25	76·38	63·40
$LiClO_4,3H_2O$	-	69·61	19·435	53·77	27·41
$NaClO_4$	113·88	35·833	1·495	36·596	8·425
$KClO_4$	2·0394	0·0830	0·0036	0·1179	0·0013
$RbClO_4$	1·328	0·0472	0·0016	0·0475	0·0014
$CsClO_4$	1·961	0·0734	0·0048	0·1178	nil
NH_4ClO_4	21·91	5·268	0·0137	1·768	0·0286

When the data are expressed as molal solubilities per mole of solvent, it is seen that the solvent capacities of the alcohols increase in the order Me > Et > *n*-Pr > *n*-Bu > *iso*-Bu. The solubility of potassium and thallium perchlorates is lower in deuterium oxide than in water.[14,15] This is no doubt the case for many other perchlorates also; for the potassium salt the ratio of the solubilities at 25° is 0·947.[15]

The compressibilities of aqueous solutions of the alkali perchlorates satisfy the equation:-

$$\Phi(K_2) = \Phi(K_2^0) + C\sqrt{c},$$

where $\Phi(K_2)$ and $\Phi(K_2^0)$ are the apparent molal compressibilities of the solution at concentration c and at infinite dilution respectively.[17] The values of C are not constant as would be required by the Debye–Hückel theory.

Molar, cationic and anionic magnetic susceptibilities have been determined for the alkali perchlorates,[18] with the results given in Table XXXVII.

TABLE XXXVII. - MAGNETIC SUSCEPTIBILITIES OF PERCHLORATES ($\times 10^6$)

Salt	Molar	Cationic	Anionic
$LiClO_4$	32·8	4·2	28·7
$NaClO_4$	37·6	9·2	28·4
$KClO_4$	47·4	18·5	28·9
$CsClO_4$	69·9	41·0	28·9
NH_4ClO_4	46·3	18·0	28·3

The thermal decomposition of lithium, sodium, potassium and calcium perchlorates has been studied,[19] and the loss in weight plotted against temperature. In each case the curve has a sharp change of slope, a feature in which these perchlorates differ from those of magnesium, iron and aluminium. The latter are converted into the oxide, and the former into the chloride.

Lithium perchlorate has been prepared electrolytically from lithium chlorate, using 0·2 amp. per sq. cm. and a temperature above 20°.[20] The product which crystallized out was the trihydrate, and this has also been obtained by the action of 70% perchloric acid on lithium carbonate.[21] The preparation of the anhydrous salt was found to be difficult; even after heating to 300° for 12 hours, the product was the anhydrous salt mixed with trihydrate. The former was extracted with ether. The solubility of lithium perchlorate in water has been determined in the temperature range 0 – 170°, and the density of the saturated solutions between 0° and 40°.[22] The transition points of the various forms are:-

$$\mathrm{LiClO_4,3H_2O} \xrightarrow{92{\cdot}53^\circ} \mathrm{LiClO_4,H_2O} \xrightarrow{145{\cdot}75^\circ} \mathrm{LiClO_4}.$$

The density of lithium perchlorate solutions is expressed by the following empirical equation:-

$$d_{15} = 0{\cdot}9913 + 5{\cdot}9396 \times 10^{-3}p + 1{\cdot}1902 \times 10^{-5}p^2 + 5{\cdot}85 \times 10^{-7}p^3,$$

where p is the g.% of the anhydrous salt.[23] The dipole moment of lithium perchlorate is 7·86 D.[24] The heat of solution of the trihydrate is –7·965 kg.-cal., and that of the anhydrous salt 6·240 kg.-cal.; thus the molar heat of hydration is 14·2 kg.-cal.[25]

The determination at 20° of the lithium perchlorate–ammonia isotherm[26] showed the presence of a diammine (dissociation pressure 2 mm.), and a triammine (dissociation pressure 39·5 mm. at 20°, and 10 mm. at 0°). A pentammine was also found with a dissociation pressure of 31 mm. at –79°.

Osmotic and activity coefficients of lithium perchlorate and sodium perchlorate have been measured at 25° over a wide concentration range.[27] While the activity coefficient of the sodium salt does not vary widely with concentration, that of the lithium salt passes through a minimum at a concentration of 0·2 molar, and then increases steeply. Cryoscopic and conductivity measurements on dilute solutions of lithium perchlorate in *cyclo*hexanol show that it behaves as a strong electrolyte.[28-30] Conductivity measurements have been made in methanol,[31] ethanol,[32] nitromethane,[33] hydrazine[34] and hydrocyanic acid,[35] showing, in general, a high mobility for the perchlorate ion and agreement with the Debye–Hückel–Onsager equation.

The influence of lithium perchlorate on the mutual solubilities of water and butyl alcohol has been determined;[36] the effect is to increase the solubility of the butyl alcohol in water at 25° to a maximum in 3·9 N-perchlorate solution, after which it decreases. This behaviour is paralleled by the calcium salt while, in contrast, the uranyl, beryllium, cadmium, zinc, magnesium, cobalt, nickel and copper salts and perchloric acid itself promote complete miscibility above 2·6 N.concentration, and the silver, lead, ammonium, strontium, barium and sodium salts decrease the solubility with increasing concentration.

Further solubility data, in addition to that quoted in Table XXXVI, have been obtained for sodium perchlorate.[37,38] This salt forms a monohydrate,[39] and at –79° a tetrammine.[26] The monohydrate is completely dehydrated at 130°, the anhydrous salt being stable in the temperature range 130 – 471°, above which decomposition occurs giving sodium chloride.[40] The existence of double salts, such as $\mathrm{NaAl(ClO_4)_4,12H_2O}$ previously reported[41] could not be confirmed.[42]

The heat of solution of sodium perchlorate in water is +3·5 kg.-cal.,[25,43] and the heat of formation of the crystalline salt is +93 kg.-cal.[44] The density of solid sodium perchlorate is 2·499, the refractive indices 1·4606, 1·4617 and 1·4731, and the molar refraction 13·58.[45] The molecular rotation (Faraday effect, for the *D* line) of sodium perchlorate increases with increasing concentration.[46] The conductivity of the salt has been measured in hydrocyanic acid,[35] hydrazine,[34] methanol[31] and ethanol.[32] Sodium perchlorate causes dispersion of gelatin.[47]

Potassium perchlorate, m.p. 610°,[48] forms no hydrate and no ammoniate;[26] the anhydrous salt is stable up to 653°.[40] Solubility data up to a temperature of 265° have been determined.[48] Solubilities in aqueous alcohol at 14° decrease from 12·4 g. per litre in water to 0·15 g. per litre in 94·7% alcohol.[49] Solubilities in various salt solutions were determined in order to evaluate activity coefficients.[50] The solubility in anhydrous hydrogen fluoride is 9·6 g. per litre.[51] The heat of solution of potassium perchlorate in water is 12·1 kg.-cal.,[43,53] a figure which has been used to evaluate the entropy and the free energy of the perchlorate ion; the heat of formation is +104·4 kg.-cal.[43] The dielectric constant of the solid is 5·9,[54] the density is 2·5298, the refractive indices 1·4717, 1·4724 and 1·476, and the molar refraction 15·37.[45]

The decomposition of potassium perchlorate to give potassium chloride and oxygen is unimolecular.[55] Ferric oxide catalyzes the reaction, its particle size increasing 5-fold during the reaction. The effects of alkali nitrites[56] and ammonium halides[57] on this decomposition have also been investigated. The former increases the rate of decomposition, while the effect of the latter appears to be due to the anion and increases with the atomic weight of the anion.

From a study of the ternary system, water–sodium chloride–potassium perchlorate, no double decomposition was found to take place between the two salts,[58] though each reduces the solubility of the other. The ternary system, potassium perchlorate–potassium fluoborate–water, gives evidence for double salts $KClO_4,nKBF_4$ where $n = 2$ and 8, which are stable in the presence of excess potassium perchlorate.[59] When a saturated solution of potassium perchlorate, sodium nitrate and sodium chloride is cooled, a mixture of the first two salts crystallizes out. The addition of water at this stage allows the crystallization of pure potassium perchlorate.[60] By the action of hydrogen in the silent electric discharge, potassium perchlorate is reduced to potassium chloride.[61] The conductivity of potassium perchlorate has been measured in hydrocyanic acid and in hydrazine.[34,35]

Rubidium perchlorate has no hydrates, and does not decompose below 400°, while cæsium perchlorate starts to decompose at 611°.[40] The entropy of cæsium perchlorate[62] at 25·0° is 41·89 ± 0·2 g.-cal. deg.$^{-1}$ mol.$^{-1}$

Ammonium perchlorate is normally prepared by reaction of sodium perchlorate with ammonium sulphate, and the carefully controlled conditions necessary are emphasized by several authors.[39,63-67] No hydrates are known, but a triammine with a dissociation pressure of 2 mm. at −79° has been reported.[26] Ammonium perchlorate has been studied as an explosive.[68] It is stable at 110°, decomposes at 130° and explodes at 380°.[69,70] At low temperatures the decomposition is: $4NH_4ClO_4 = 2Cl_2 + 8H_2O + 2N_2O + 3O_2$. Above 400°, most of the nitrogen is evolved as nitric oxide.[70] A suitable mixture for use as an explosive was prepared by mixing concentrated solutions of ammonium nitrate and sodium perchlorate at about 140° and allowing crystallization to take place.[71]

The solubility of ammonium perchlorate in ammoniacal solutions at 25° increases from 21·63 g.per 100 c.c. of solution in 0·443 N-ammonium hydroxide to 24·08 g. in 2·59 N.solution.[72] The density of aqueous solutions of ammonium perchlorate at 15° and 25° can be expressed by the following equations:-[73]

$$d_{15} = 0{\cdot}99913 + 4{\cdot}6826 \times 10^{-3}p + 1{\cdot}425 \times 10^{-5}p^2 + 2{\cdot}10 \times 10^{-7}p^3$$

$$d_{25} = 0{\cdot}99707 + 4{\cdot}7898 \times 10^{-3}p + 1{\cdot}920 \times 10^{-5}p^2 + 1{\cdot}33 \times 10^{-7}p^3$$

where p is the g.% of the anhydrous salt. At 25°, solution of ammonium perchlorate in water produces an increase in volume, but a decrease at 15°. The solubility of ammonium perchlorate is less in aqueous perchloric acid solution than in water.[37]

The conductivities of ammonium perchlorate in anhydrous hydrocyanic acid[75] and nitromethane[33] show agreement with the Debye-Hückel-Onsager equation. The solubility in liquid ammonia is 137·93 g. per 100 g. of liquid ammonia,[76] and the dissociation constant $5{\cdot}4 \times 10^{-3}$.[77] A number of compounds have been prepared by the reaction of aqueous solutions of antipyrine and ammonium perchlorate with solutions of various metal salts. The products are crystalline and of a colour dependent on that of the cation. These are formulated as $[M(COC_{10}H_{12}N_2)_6](ClO_4)_2$, where M = Mg, Ca, Sr, Ba, Zn, Cd, Pb, Mn, Fe^{II}, Co and Ni etc. Silver gave a tri-antipyrine compound. The melting points and solubilities of the various compounds are recorded.[126]

The heat of solution of ammonium perchlorate in water is +6·36 kg.-cal. and the heat of formation +70·2 kg.-cal.[43] The density of the solid is 1·9518, the refractive indices, 1·4824, 1·4828 and 1·4868, and the molar refraction 17·22.[45] The dielectric constant of the crystals decreases regularly with temperature.[74]

A method for preparing the Group II perchlorates by the reaction of their oxides and carbonates with ammonium perchlorate in the solid state has been described.[78] Reaction was more rapid and took place at a lower temperature the more basic was the metal. Neither pressing the materials together nor decreasing the particle size affected the yield, though this was improved by making the layer of reactants as shallow as possible. The extent of reaction increases with the stability of the perchlorate ammine, which is an intermediate product. The products are not pure; in the case of calcium perchlorate, only 30% purity is obtained, but the products are suitable for use in fireworks.[78,79]

Solubility data for the alkaline earth metal perchlorates are presented in Table XXXVIII.[13]

TABLE XXXVIII.- SOLUBILITIES OF ALKALINE EARTH METAL PERCHLORATES (g./100 c.c.SOLUTION)

Salt	Water	MeOH	n-BuOH	$COMe_2$	AcOEt
$Mg(ClO_4)_2$	73·453	37·749	44·638	32·410	54·173
$Ca(ClO_4)_2$	112·34	113·68	68·419	43·812	57·173
$Sr(ClO_4)_2$	157·51	113·95	71·205	89·92	76·67
$Ba(ClO_4)_2$	128·99	119·85	41·716	81·054	80·812

When the data are expressed as molal solubilities per mole of solvent, it is seen that the Group II perchlorates are more soluble in organic solvents (except ether) than in water.

Various ammines of the Group II perchlorates have been identified from studies of their isotherms with ammonia.[80-82] They correspond to $M(ClO_4)_2$, $n\,NH_3$; n = for Mg, 2, 6 and 7; for Ca, 2, 3, 4, 6 and 7; for Sr, 1, 2, 6, 7, 10 and 12; for Ba, 2,5,6 and 9. Pyridine complexes are also formed by these perchlorates in the presence of liquid pyridine or its vapour.[83] They decompose in a desiccator, or over concentrated sulphuric acid. In crystal form and solubility they differ widely from the parent perchlorate. The compounds of magnesium, calcium, strontium and barium are all colourless, hygroscopic solids corresponding to the formula $M(ClO_4)_2,6(C_5H_5N)$.

Magnetic susceptibilities,[18] and heats of hydration,[28] are given in Table XXXIX.

TABLE XXXIX. - MAGNETIC SUSCEPTIBILITIES AND HEATS OF HYDRATION FOR THE ALKALINE EARTH PERCHLORATES

Perchlorate	Susceptibilities ($\times 10^6$)			Heat of hydration (kg.-cal.)	No. of H_2O molecules
	Molar	Cationic	Anionic		
$Mg(ClO_4)_2$	65·0	10·1	27·5	38·370	6
$Ca(ClO_4)_2$	70·5	16·0	27·2	15·485	4
$Sr(ClO_4)_2$	81·4	24·5	28·5	13·200	4
				9·500	2
$Ba(ClO_4)_2$	94·7	38·2	28·3	8·630	3

Aqueous solutions of all the Group II perchlorates have been used as solvents for cellulose.[47,84]

Magnesium perchlorate, both as the trihydrate and as the anhydrous salt ('anhydrone'), is much used as a drying agent. The efficiency of both forms has been assessed and compared with that of other desiccants.[85] The numbers of mg. of water remaining per litre of dried air are: calcium chloride (granular) 1·5, barium perchlorate, 0·82, calcium chloride (anhydrous) 0·36, magnesium perchlorate trihydrate 0·31, silica gel 0·006, anhydrous magnesium perchlorate 0·002, barium oxide 0·00065. The usual preparation is by metathesis, e.g. from ammonium perchlorate and magnesium carbonate, followed by heating in a vacuum if the anhydrous salt is required.[86-89] Though the procedure is normally considered safe, warnings of the risk of explosion in contact with organic materials have been given.[90,91] A mixture of magnesium perchlorate and barium perchlorate has also been suggested as a desiccant.[92] The density of magnesium perchlorate decreases from 2·60 for the anhydrous salt to 2·044 for the trihydrate, and 1·970 for the hexahydrate;[93] it has been claimed that the trihydrate is not a definite compound, but mixed crystals,[94] though this view is not commonly held. A dihydrate and tetrahydrate have also been described.[95]

The solubility of magnesium perchlorate in ether has been variously reported as 0·29%,[13] 0·06%[96] and 20 – 25%,[21] all at 25°. The high values may be attributed to the presence of moisture.[96] Three etherates have been reported; a tri-etherate unstable at 0°, a di-etherate fairly stable at 25°, and a monoetherate stable above 100°.[96] The solubility of many organic compounds in water is increased by magnesium perchlorate.[97] This, however, is a common property of a number of perchlorates, and is comparatively little affected by the cation.

The structure of magnesium perchlorate hexahydrate is hexagonal and related to that of lithium perchlorate trihydrate.[98] The axes of the unit cell are 15·52 A. and 5·26 A. Activity and osmotic coefficients,[99] Raman spectra frequencies,[100] and conductivities in acetone, methanol, nitromethane[101] and *n*- and *iso*- propanols,[102] have been determined.

The basic salts $3Ca(OH)_2,Ca(ClO_4)_2,12H_2O$ and $Ca(OH)_2,Ca(ClO_4)_2,2-4H_2O$ have been prepared, but no specific properties have been described.[103] The conductivity of calcium perchlorate in acetone,[101] and the coefficients of adiabatic compressibility of aqueous solutions of calcium and strontium perchlorates have been determined.[104] The apparent molar compressibility varies with the square root of concentration. Solvation increases with dilution and is calculated to be $11H_2O$ for the calcium salt and $13H_2O$ for the strontium salt.

Barium perchlorate has been prepared from ammonium perchlorate and baryta;[105] and the preparation of the trihydrate and its use as a desiccant have been described.[106] All the ammines, $Ba(ClO_4)_2,nNH_3$, where $n = 2, 5, 6$ and 9, are soluble in liquid ammonia and in ethanol.[107] There is also a basic salt, $Ba(OH)ClO_4$.[108] The heat of solution of barium perchlorate is +1·42 kg.-cal., and the heat of formation +194·3 kg.-cal.;[43] the density of the trihydrate is 2·911, the refractive indices 1·533 and 1·532, and the molar refraction 41·60.[45]

Five different hydrates of aluminium perchlorate have been described, as well as the anhydrous salt; these are $Al(ClO_4)_3,n\ H_2O$ where $n = 3, 6, 9, 12$ and 15. The 15- hydrate is prepared by adding excess of aluminium hydroxide to perchloric acid and crystallizing on a steam bath.[109] It is non-hygroscopic, loses 3 mols. of water in a desiccator over concentrated sulphuric acid, and at 100° is converted into the hexahydrate: its solubility in water is 6·86% at 18·5° and 42·27% at 90°. The 9- hydrate can be prepared by crystallization of the solution after aluminium has been dissolved in 70% perchloric acid.[110] It has a very high solubility; 462·75 g. per 100 g. of water at 0°.[111] Other workers failed to obtain the 12- hydrate,[112] and represent the preparation of the other hydrates thus:-

$$15H_2O \xrightarrow{\text{(at }18^\circ\text{ over conc. }H_2SO_4)} 9H_2O \xrightarrow{(18^\circ\text{ over }P_2O_5)} 6H_2O \xrightarrow{} 3H_2O \xrightarrow{(150^\circ\text{ in vacuum over }P_2O_5)} \text{Anhydrous}$$

TABLE XL. - DENSITIES AND MELTING POINTS OF THE HYDRATES OF ALUMINIUM PERCHLORATE[110]

	Density	Melting point
$Al(ClO_4)_3,15H_2O$	1·764	76·2°
$Al(ClO_4)_3,\ 9H_2O$	1·924	85·3°
$Al(ClO_4)_3,\ 6H_2O$	2·020	120·8°
$Al(ClO_4)_3,\ 3H_2O$	2·145	-
$Al(ClO_4)_3,\ 0H_2O$	2·209	-

An alternative method of preparing anhydrous aluminium perchlorate involves distilling anhydrous perchloric acid on to anhydrous aluminium chloride and removing excess acid in a current of nitrogen;[113] the product is slightly contaminated with aluminium chloride but can be purified by recrystallization from organic solvents, in which it is very soluble. Electrolysis of solutions in Cellosolve, nitromethane and nitrobenzene did not yield any metallic aluminium.[113,114] Solutions of aluminium and chromium perchlorates show an unexpectedly high hydrogen ion activity even in very dilute solution. No change takes place on standing, showing that no complex formation occurs.[115] The Raman spectra have been studied.[100]

Gallium perchlorate hexahydrate was first prepared in 1939,[116,117,119] by dissolving gallium metal in hot concentrated perchloric acid, followed by crystallization. It is very deliquescent, very soluble in water, acetic acid and alcohol, and decomposes at 155° in a vacuum and at 175° at atmospheric pressure. Using an excess of perchloric acid a 9·5- hydrate was obtained; other workers consider it to be the 9- hydrate.[118] This product loses 3 molecules of water on standing over concentrated sulphuric acid. A complex with urea, $Ga[CO(NH_2)_2](ClO_4)_3$, is formed by interaction of the perchlorate and urea in non-aqueous solvents;[118] this decomposes violently on heating. Attempts to dehydrate the 6- hydrate produce a basic salt, and not the anhydrous perchlorate. No further work on indium perchlorate has been described.

The structure of thallium perchlorate has been studied by *X*-ray methods. It is isomorphous with the perchlorates of the Group I metals, except lithium, having cell dimensions 9·42, 5·88 and 7·50 A. respectively.[5] The space group is V_h^{16}. A cubic form of the compound was found to have space group T_d^2 or T^2 with cell dimension 7·61 A.[8] A transition from the ordinary rhombic to a regular isotropic form occurs at 266°.[16] Conductivities have been measured for thallium perchlorate in water,[120] and in nitromethane.[33] In water the dissociation constant is 1·00 at 25° for 0·002 - 0·005 M.solutions.[120] Sedimentation equilibria[121] and activity coefficients[122] have been determined.

The $Tl^+ \rightarrow Tl^{3+}$ potential in perchloric acid and in nitric acid solutions has the same value, 1·280 V.[123] Absorption spectra of the two ions in perchloric acid solution show Tl^{III} to be more highly coloured than Tl^I.[124] Extinction coefficients illustrate the increased tendency to undergo hydrolysis, $Tl^{3+} \rightarrow Tl(OH)^{2+} \rightarrow Tl(OH)_2^+$, as the acidity of the solution decreases. Densities and refractive indices of solid thallium perchlorate have been measured.[125] The existence of the ion ClO_4^- in anhydrous hydrofluoric acid has been deduced from precipitation reactions of thallous perchlorate in hydrofluoric acid solution.[51]

An unsuccessful attempt to prepare germanium perchlorate has been described.[127] The hydrolysis of Sn^{2+} in stannous perchlorate has been investigated by potentiometric means. Assuming that hydrolysis gives $[Sn_2(OH)_2]^{2+}$ or $[Sn_2O]^{2+}$, the hydrolysis constant is $1{\cdot}8 \times 10^{-3}$ at 25°.[128] If the hydrolysis is considered to be $Sn^{2+} + H_2O \rightarrow Sn(OH)^+ + H^+$, the constant is 0·02 at 25°.[129]

Lead perchlorate has been prepared in the anhydrous state, and as the mono- and tri- hydrate.[130] When lead nitrate is dissolved in perchloric acid, and the liberated nitric acid distilled off, crystallization yields the trihydrate, m.p. 83 - 84°. When this is kept for several months in a vacuum over phosphoric oxide at 65°, the anhydrous salt is obtained. Its solubility is 226·1 g. per 100 c.c. of solution, and the density of the saturated solution is 2·773 at 25°. The use of these solutions for determining densities by the suspension method has been suggested.[131] The monohydrate was prepared from the trihydrate by keeping it first over phosphoric oxide and then over anhydrous lead perchlorate for months in a vacuum; its m.p. is 153 - 155°. Interaction of lead oxide with perchloric acid leads to the formation of basic salts. A number of these have been described, e.g. $[Pb_2(OH)_2](ClO_4)_2, 1{\cdot}5\ H_2O$ and $[Pb_3(OH)_4](ClO_4)_2$.[132] Complexes containing lead in the anion have also been described, e.g.:-

$$\mathrm{Na[Pb^{(ClO_4)}_{(OAc)_2}]} \text{ and } \mathrm{Na[Pb_2{}^{(ClO_4)}_{(OAc)_4}]};$$

also a complex in which lead is present in both anion and cation, $[Pb_4(OAc)_6][Pb(ClO_4)_4], 3H_2O$.[133] The dissociation of $[Pb_2(OH)_2](ClO_4)_2$ is governed by the equilibria:-

$$\begin{aligned}[Pb_2(OH)_2](ClO_4)_2 &\rightleftharpoons [Pb_2(OH)_2]^{2+} + 2(ClO_4)^- \\ &\rightleftharpoons Pb^{2+} + 2(ClO_4)^- + Pb(OH)_2.\end{aligned}$$

In dilute solution the reaction proceeds to the right, precipitating lead hydroxide.[134] Neutralization curves of lead perchlorate have been interpreted as showing that plumbous salts hydrolyze in accord with the equations:-

$$\begin{aligned}&(1)\quad Pb^{2+} + H_2O \rightleftharpoons [PbOH]^+ + H^+ \\ &(2)\quad 4Pb^{2+} + 4H_2O \rightleftharpoons [PbOH]_4^{4+} + 4H^+.\end{aligned}$$[135]

Anhydrous nitric acid and perchloric acid react at a low temperature giving solid nitracidium perchlorate, $[H_3NO_3]^{2+}(ClO_4^-)_2$.[136] By fractional crystallization from nitromethane this is separated into nitronium perchlorate, $[NO_2^+](ClO_4^-)$, and perchloric acid monohydrate. Nitronium perchlorate has a very low vapour pressure and dissolves in water with slight liberation of heat. Raman spectra consist of the sum of the known spectra of NO_2^+ and ClO_4^-. Interaction of phosphoric and perchloric acids gives a compound formulated as $P(OH)_4ClO_4$. It forms orthorhombic crystals, m.p. 46 - 47°. Its conductivity in nitromethane shows the presence of perchlorate ions. The heat of solution in that solvent is 13·9 kg.-cal. per mol., and the heat of formation 11·4 kg.-cal. per mol.[137,138] Freshly precipitated $Sb(OH)_3$ dissolved in warm 70% perchloric acid yields crystalline antimony oxyperchlorate trihydrate, $SbOClO_4$, $3H_2O$. This compound decrepitates when heated above 60°, yielding oxides of antimony: it is hydrolyzed by water.[139] Several workers[139-141] have pointed out the danger of trying to prepare bismuth perchlorate by the solution of bismuth metal in perchloric acid.[142] Reaction of bismuth oxide and perchloric acid, with constant removal of water, yields bismuth perchlorate pentahydrate,[139] while from more dilute solutions $BiO(ClO_4),3H_2O$ and $BiO(ClO_4),H_2O$ are obtained. The monohydrate can be rendered anhydrous by heating to 80 - 100°, and its conductivity is that of a uni-univalent salt, possibly $[Bi(OH)_2]^+(ClO_4^-)$.[143] Conditions for the stability of the basic salts are described.[144] The potential between the N.H-electrode and a bismuth electrode in a molar solution of bismuth perchlorate is 0·289 V.[145] Some Raman spectrum frequencies have been determined for both $Bi(ClO_4)_3$ and $BiOClO_4$.[100]

A compound $Se(OH)_3ClO_4$ has been prepared by adding selenious acid to ice-cold perchloric acid, warming slightly to ensure solution and re-cooling to allow crystallization. The crystals are monoclinic and very deliquescent. As with the corresponding phosphorus compound, the presence of the ion $Se(OH)_3^+$ is shown by conductivity measurements in nitromethane; the heats of solution and formation are 4·8 and 11·4 kg.-cal. per mol., respectively.[138]

Hydrofluoric acid forms with perchloric acid a stable compound $[FH_2]^+ (ClO_4)^-$.[146] The corresponding chlorine compound decomposed spontaneously with violence. Fluorine reacts with concentrated perchloric acid to yield the compound $FClO_4$, m.p. -167·3° and b.p. -15·9° at 755 mm.[147] (See page 184). It is said to have a sharp irritating smell and to be highly reactive and explosive. Its reactions with I^- and OH^- are as follows:-

$$FClO_4 + 2I^- \rightarrow I_2 + ClO_4^- + F^-,$$
$$\text{and } 2FClO_4 + 4OH^- \rightarrow O_2 + 2ClO_4^- + 2F^- + 2H_2O.$$

The perchlorates of the transition metals have not been investigated so thoroughly as those already described. The solubility of the perchlorates of lanthanum and the lanthanide elements has been investigated with a view to a possible method for the fractional crystallization of these metals in alkaline solution.[148] Some hexa-antipyrine complexes, $M(COC_{19}H_{12}N_2)_6(ClO_4)_3$, have been examined for the same reason, and their properties are given in Table XLI.

TABLE XLI. - PROPERTIES OF PERCHLORATES OF ANTIPYRINE COMPLEXES OF LANTHANIDE ELEMENTS[148]

Metal	Appearance	M.p.°	Solubility (g./100 c.c. solution at 20°)
La^{3+}	Colourless, hexagonal	290 - 295	1·48
Ce^{3+}	Colourless, hexagonal	295 - 300	1·07
Nd^{3+}	Rose, hexagonal	285 - 289	0·98
Pr^{3+}	Green, hexagonal	286 - 291	-
Y^{3+}	Colourless, hexagonal	293 - 296	0·55

An attempt to prepare solid ceric perchlorate by concentration of its aqueous solution was unsuccessful.[149] The product was a basic salt, probably $Ce_2O_3(ClO_4)_2$, 12 H_2O. An aqueous solution of the salt was prepared by electrolytic oxidation of a solution of cerous perchlorate. Ceric perchlorate undergoes photochemical reduction in 2 M-perchloric acid on exposure to light of 310 mμ, and oxygen is evolved.[150] The reaction is heterogeneous, taking place on the walls of the containing vessel. The yield of oxygen is increased by packing the vessel, but is decreased by increasing the concentration. Spectrophotometric studies of ceric perchlorate solutions show no evidence of the formation of any coloured complex ions:[151] the solutions obey Beer's law up to a concentration of 0·01 M. A study has also been made of the thermal reaction between the ceric ion and water in perchloric acid solution.[152] Neodymium perchlorate hexahydrate has been prepared by the solution of Nd_2O_3 in perchloric acid.[148] At 170° the water of crystallization can be removed, leaving a hygroscopic solid. The molar refraction and absorption spectra of its aqueous solution have been investigated.[153] Gadolinium perchlorate octahydrate has been prepared.[154,155] It is a deliquescent solid, very soluble in water and in alcohol. Raman spectra and frequency measurements on aqueous solutions of lanthanum perchlorate have been compared with those on other trivalent metal perchlorates.[100]

A solution of vanadium^{III} perchlorate, blue in colour, is obtained by electrolyzing a suspension of vanadium pentoxide in perchloric acid for 48 hours in an atmosphere of nitrogen.[156] Its absorption spectrum has been determined and analyzed into separate absorption curves for the V^{3+} ion and its hydrolysis product $(VOH)^{2+}$. The heat of the hydrolysis, $V^{3+} \rightarrow (VOH)^{2+}$, is 10 ± 1 kg.-cal. at room temperature. Green crystals of chromium perchlorate are said to be formed after some time in a reaction mixture in which chromic oxide has been dissolved in perchloric acid.[157] Chromic hydroxide reacts with perchloric acid to give chromic perchlorate, and a number of hydrated forms have been described, *i.e.* $Cr(ClO_4)_3,n\ H_2O$, where $n = 3, 5, 6, 9, 10$ or 21.[158,159]

A hydrated form of manganese perchlorate, probably a hexahydrate, was prepared by dissolving manganese carbonate in perchloric acid, followed by filtration and crystallization.[160] The compound melted (with some decomposition) at 165°; decomposition was rapid at and above 230°, the products being oxygen, manganese dioxide and chlorine oxides. No anhydrous salt was obtained.

The crystal structures of the perchlorates of Mn, Fe, Co, Ni, Zn and Cd hexahydrates have been investigated,[98] and shown to resemble that of lithium perchlorate trihydrate. The relevant data are given in Table XLII.

TABLE XLII. - CRYSTAL STRUCTURES OF SOME TRANSITION METAL PERCHLORATES

Metal M in $M(ClO_4)_2,6H_2O$	Refractive indices		Cell dimensions (Hexagonal system)	
	n_0	n_e	a	c
Mn	1·492	1·475	15·70 A.	5·30 A.
Fe	1·493	1·478	15·58	5·24
Co	1·510	1·490	15·52	5·20
Ni	1·518	1·498	15·46	5·19
Zn	1·508	1·487	15·52	5·20
Cd	1·489	1·480	15·92	5·30

Mercury and copper perchlorates are trigonal and monoclinic respectively.

The preparation, analysis and hydrolysis of iron perchlorates have been described in a series of papers.[161-164] Ferrous perchlorate hexahydrate was prepared as long green crystals by adding 70% perchloric acid to ferrous sulphide in an atmosphere of carbon dioxide or nitrogen. The compound is stable in air, but loses one molecule of water over 90% sulphuric acid, two molecules over 95·6% acid, and four molecules over 96% acid in a vacuum. Its solubility in water rises from 978 g. per litre at 0° to 1161 g. per litre at 60°, and its solubility in ethyl alcohol is 8654 g. per litre: the solubility in perchloric acid solution passes through a minimum at 9·30 M.acid. Ferrous perchlorate is easily oxidized in solution, hydrolysis occurring according to the equation:-

$$Fe^{2+} + H_2O \rightleftharpoons FeOH^+ + H^+.$$

Ferric perchlorate decahydrate was prepared by heating ferric hydroxide with 70% perchloric acid on a water bath under reflux for 10 hours. It loses one molecule of water over 75% sulphuric acid, and four over concentrated sulphuric acid or phosphorus pentoxide. Its solubility in water is 1198 g./litre at 0° and 1517 g./litre at 60°. There is no minimum in the curve of its solubility in perchloric acid solutions.[161] The hydrolysis constant decreases with increasing concentration, and the heat of hydrolysis is 18·2 kg.-cal.[163] At a given perchloric acid concentration, the hydrolysis equilibrium depends on concentration of perchlorate ion.[165] The attainment of equilibrium in the reaction:-

$$2Fe(ClO_4)_3 + 2Hg \rightleftharpoons 2Fe(ClO_4)_2 + Hg_2(ClO_4)_2$$

is catalyzed by kieselguhr and various forms of active carbon, some of which can bring about equilibrium within one minute.[166] The equilibrium constant is 0·539 at 35° and infinite dilution, and $\Delta H = 20$ kg.-cal./mol.[167] The kinetics of the reaction between ferric and stannous perchlorates in acid solution have also been studied.[168] The rate-determining step is the reaction between $Fe(OH)^{2+}$ and Sn^{2+}. From the behaviour of ferrous and ferric perchlorates in perchloric acid solution, it has been shown that the Fe^{2+} ion diffuses more rapidly than Fe^{3+};[169] the diffusion coefficient of ferric perchlorate has been measured.[170] Some reduction of ferric perchlorate to the ferrous state by ultra-violet light has been observed from a study of absorption curves when this salt is dissolved in a number of solvents.[171] Absorption curves for ferric perchlorate in the presence of hydroxyl, chloride and bromide ions are recorded, and the absorption curve for free ferric ions has been deduced.[172] Absorption of light by acid solutions of ferric perchlorate is thought to be due to the presence of $[Fe(H_2O)]^{3+}$[173] A number of complex compounds containing iron and the perchlorate ion have been prepared and studied;[174] these include:- $[Fe_3(CH_2ClCOO)_6(OH)_2](ClO_4),9H_2O$, $[Fe_3(OOC.CH_2COO)_3(OH)_2]ClO_4$, $[Fe_3(CH_2\text{-}(OH)COO)_6(OH)_2]ClO_4,NaClO_4,4H_2O$, and $[Fe_3(OOC.CH_2CN)_6(OH)_2]ClO_4,8H_2O$.

Cobaltic perchlorate has been prepared from cobaltous perchlorate, both electrolytically and by the action of fluorine.[175] The yield is poorer in the latter case, and passes through a maximum when yield is plotted against time. This is presumably due to reduction by hydrogen peroxide formed in a side reaction. Using cobalt perchlorates in water labelled with $H_2^{18}O$, it has been shown that the hydrated cobalt^{II} and cobalt^{III} ions exchange water molecules with the aqueous solvent.[176] Pyridine complexes may be prepared by reaction of the metal perchlorate with pyridine.[83] These are $M(ClO_4)_2,nC_5H_5N$, where $n = 6$ for M = Co, Ni, Hg and Cd; $n = 4$ for M = Cu and Zn; and $n = 8$ for M = Mn.

The light absorption of solutions of nickel perchlorate has been studied.[177] The extinction coefficient shows continuous absorption in the violet region with a maximum in the red: dilution shifts the maximum towards shorter wavelengths. The hydrolysis of nickel perchlorate in aqueous solutions is accelerated by light.[178] The deposition potential of Ni from N. solutions of nickel perchlorate is −0·49 V.[179]

For zinc perchlorate, osmotic and activity coefficients have been determined:[99,180] the salt is found to be normally dissociated, in contrast to the zinc halides. Both zinc and cadmium perchlorates form tetra- and hexa-ammoniates.[80] The solubility of cadmium oxalate is increased as cadmium perchlorate is added to its solution: this is attributed to the existence of an ion $CdC_2O_4.Cd^{2+}$.[181] A study of solubilities in the system mercurous perchlorate–water shows the existence of two hydrates, with 2 and 4 molecules of water respectively.[182] Hydrolysis of mercurous perchlorate takes place in three stages:-

$$Hg_2(ClO_4)_2 \rightarrow Hg_2O.Hg_2(ClO_4)_2 \rightarrow Hg_2(OH)ClO_4 \rightarrow Hg_2O.$$

Mercurous perchlorate can be used as a volumetric reagent in determinations of iron:[183] the procedure is to add potassium thiocyanate to the ferric solution, and titrate with mercurous perchlorate until the red colour disappears.

Cupric perchlorate is prepared by dissolving basic copper carbonate in perchloric acid. Crystallization gives a heptahydrate,[184] which is converted into the hexahydrate when kept over phosphoric oxide. This appears to be the most stable form, though tetra- and di- hydrates have also been described. The hexahydrate has m.p. 82·3°;[185] its solubility is 54·3% in water at 23°, the density of the solution being 2·225, the molar heat of solution -4·6 kg.-cal. and the heat of formation in solution 64·7 kg.-cal.[184] Various ammoniates including $Cu(ClO_4)_2,5NH_3,2H_2O$ and $3Cu(ClO_4)_2,10NH_3$ have been described.[186] A basic copper perchlorate is formulated as $Cu(ClO_4)_2,6CuO,H_2O$ on electrometric evidence,[187] and solubility products for a number of basic cupric perchlorates have been calculated.[188] Because of its greater stability, cupric perchlorate solution is said to be preferable to that of potassium iodate when used as a volumetric standard.[189] Concentrated solutions of copper perchlorate do not obey Beer's law.[190]

Silver perchlorate is prepared by treating silver nitrate with perchloric acid, and heating to remove the nitric acid: excess perchloric acid is removed in a vacuum at 150°, and recrystallization from water (to remove any silver chloride) then gives a monohydrate. At 43°, dehydration to the anhydrous salt occurs. This is very deliquescent, and should be stored in the dark over anhydrone. It is very light-sensitive when pure, but less so in the presence of a trace of perchloric acid. Silver peroxide dissolves in perchloric acid with the formation of silver perchlorate and the liberation of oxygen.[204] The solubility in water ranges from 82·07% at 0° (density of saturated solution 2·7251) to 86·21% at 35° (d_{sat} = 2·9173). The solubilities of anhydrous silver perchlorate in 60 - 73·6% perchloric acid at 0° and 25° have also been reported.[191] The densities of aqueous solutions at 15° can be expressed by the empirical equation:-

$$d_{15} = 0{\cdot}99913 + 7{\cdot}9183 \times 10^{-3}p + 8{\cdot}762 \times 10^{-5}p^2 - 5{\cdot}35 \times 10^{-7}p^3$$

where p is the g.% of anhydrous salt.[23] The heats of dilution of aqueous solutions have been discussed in the light of the Debye-Bjerrum theory.[193] Silver perchlorate has the space group T_d or T, and a cell dimension of 6·92 A.[8] A transition from the ordinary rhombic form to a regular isotropic form occurs at 155 - 159°.[16]

Silver perchlorate is remarkable for its high solubility in non-aqueous solvents, for example chlorobenzene, toluene, nitrobenzene, acetic acid, glycerol and benzene.[194] In benzene (solubility 53 g. per litre) silver perchlorate exists in several different polymeric forms, depending on concentration,[194,195] and in dilute solution is present as ion-pairs. This is confirmed by measurements of the molar polarization[196] and conductivity.[197] The dipole moment of silver perchlorate in N/200 concentration in benzene is 4·7 D at 25°,[192] increasing on dilution (to N/5000) to 10·7 D, which is close to the theoretical value for the ion pair.[206] Silver perchlorate is also associated in benzene-acetic acid mixtures.[198] The high solubility of silver perchlorate in these solvents is no doubt a consequence of its ability to form unusual addition compounds. From benzene solution the solid phase $AgClO_4,C_6H_6$ can be isolated. These compounds are liable to explode when struck.[203]

The binary systems of silver perchlorate with aniline,[199] with toluene,[200] and with pyridine,[201] have been studied. In the aniline system, the compounds

$AgClO_4,nPhNH_2$, where $n = 1, 2, 3$ and 6, are described. Below 22·6° the solid phase isolated from toluene solution is the compound $AgClO_4,C_7H_8$. The high solubility (50·3% at 25°) indicates that this compound is stable in solution. The pyridine system gave the compounds a $AgClO_4,b$ C_5H_5N, where $a:b = 1:2$, $1:4$ and $4:9$. The solubility of silver perchlorate in pyridine varies from 4·0% at −41·5° to 50·0% at 110°. Electrical conductivities for silver perchlorate have been measured in methanol,[31] ethanol,[32] nitromethane[33] and nitrobenzene.[202] Silver perchlorate is ionized in anhydrous hydrofluoric acid,[51] and in hydrocyanic acid,[52] as it is in any medium of high dielectric constant.

Solutions of silver perchlorate absorb much more acetylene before a permanent precipitate of silver acetylide is formed than do equivalent solutions of silver nitrate.[205] This is thought to be due to the formation of a complex of the type $(C_2Ag_2)_n(Ag^+)_p$ with $p \geqslant 4n$.

Uranyl perchlorate has been prepared by interaction in water of equivalent amounts of barium perchlorate and uranyl sulphate, followed by evaporation.[207] The crystals appeared to be rhombic; they give yellow solutions in water, alcohol, ether and chloroform, but are insoluble in carbon disulphide. Attempts at recrystallization from ethanol resulted in an explosion. UO_2^{2+} is the only stable ion of hexavalent uranium in aqueous perchlorate solutions at low pH.[208] At pH > 3·0, hydrolysis is considerable. A study of the equilibrium, $UO_2^+ \rightleftharpoons UO_2^{2+} + e$, and the disporportionation of the ion UO_2^+ has been carried out in solutions of the perchlorates.[209] Perchlorates of 4-, 5- and 6- valent neptunium have been prepared in solution.[210] Trivalent plutonium forms a perchlorate which is readily soluble in dilute acids giving a bright blue solution.[211]

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SECTION XVIII

SPECTROSCOPY OF CHLORINE, BROMINE AND IODINE CHLORIDES, HYDROGEN CHLORIDE AND CHLORINE OXIDES, OXYACIDS AND IONS

By R. F. BARROW

THE CHLORINE ATOM

Optical Spectra.

The following Table gives a list of the more important work on the optical spectra of the chlorine atom.

Spectrum	λλ, A.	Notes	Reference
I	-	Zeeman effect	1,2
I,II	-	Note on multiplets	3
I,II	2070 - 3354	-	4
I,II	2070 - 3522	-	5
I - III	3602 - 4819	-	6
I,II	-	Note on multiplets	7
I	1230 - 2050	-	8
I	-	Note on analysis	9
I,II	-	Stark effect	10
I	4200 - 4700	-	11
I	4000 - 9900	-	12
I	4225 - 8700	-	13
I	3900 - 5000	Stark effect	14
I,II	2000 - 6600	-	15
I	3000 - 12000	-	16
I	-	-	17
I	3690 - 9200	Zeeman effect	18
II	-	Note on u.v. multiplets	19
II,III	2200 - 6850	-	20,21
II	1300 - 2250	-	22
II - V	390 - 3850	-	23
II	2321 - 6759	-	24
II	2495 - 5457	-	25
II	2251 - 4785	-	26
II	2544 - 8393	-	27
II	3096 - 6713	-	28
II	2100 - 9483	-	29
II	-	-	30
III	-	-	31
III	-	Note on multiplets	32
II,III	2469 - 5475	-	33
III	-	Note on quartets	34
III - V	286 - 5000	-	35
IV	331 - 757	-	36
IV,V	-	-	37
V	538 - 639	-	38
V	671 - 724	-	39

Spectrum	λλ, A.	Notes	Reference
V,VI	236–580	-	40
VI	194–736	-	41
VII	800–813	-	42
VII	174–813	-	43
VIII–XI	39–60	-	44
VIII	-	Theoretical: Vector Coupling	45

The analyses of these spectra are collected in the tables of Moore.[46] Summaries of wave-lengths are given in the Multiplet Tables of Princeton University[47] for $\lambda > 3000$ A., and in the Ultra-violet Multiplet Table of Moore[48] for $\lambda < 3000$ A. An atlas[49] containing charts of Cl I and II lines has been published.

Hyperfine structure in chlorine spectra has been reviewed.[50] Jenkins[51] found isotope shifts of the order of 0·001 A.: Tolansky[52] found that the separation between ^{35}Cl and ^{37}Cl in the line $4s\,^5S_2 - 4p\,^5P_2$ of Cl II was 0·035 cm.$^{-1}$ Some of the interpretation of the earlier work[52,55,56] is incorrect, for the nuclear spins of ^{35}Cl and of ^{37}Cl were wrongly taken to be 5/2, following the results of the difficult measurement of the intensity alternation in the band-spectrum of Cl_2.[53,54] Analysis of the microwave spectra of chlorine-containing compounds has led to the accurate evaluation of a number of properties of the chlorine nuclei. The detailed interpretation of the absorption spectrum of ClCN established[57] that the nuclear spins of ^{35}Cl and of ^{37}Cl are both 3/2: the values of the nuclear quadrupole moments were also found. This information has been confirmed by studies of other molecules, in particular methyl chloride.[58-60] Hyperfine structure in the microwave spectrum of cyanogen chloride (^{36}Cl) has been analysed[61] to give the nuclear spin and the nuclear quadrupole moment of this isotope. The atomic beam magnetic resonance method has been used[62] to investigate the hyperfine structure of the $^2P_{3/2}$ ground-states of ^{35}Cl and ^{37}Cl.

The following values of nuclear properties have been taken largely from the review of microwave spectroscopy by Gordy, Smith and Trambarulo.[63]

	Nuclear spin	Statistics	Mass atomic mass units	Nuclear magnetic moment (nuclear magnetons)	Quadrupole moment cm^2 × 10^{-24}
^{35}Cl	3/2	Fermi	34·97867	0·82191	−0·07894
^{36}Cl	2	-	-	-	−0·0168
^{37}Cl	3/2	Fermi	36·97750	0·68414	−0·06213

The ground state of the chlorine atom is an inverted doublet, with $^2P_{1/2}$ lying at about 881 cm.$^{-1}$, or[64] 882·5 cm.$^{-1}$, above $^2P_{3/2}$. There are no very low-lying excited states. The term-values of Moore[46] and of Avellén[64] for the lowest states are given below.

		Moore	Avellén
$3s^23p^44s$	$^2P_{1/2}$	74861·24	74865·7
	$^2P_{3/2}$	74221·44	74225·9
	$^4P_{1/2}$	72822·64	72827·1
	$^4P_{3/2}$	72484·20	72488·7
	$^4P_{5/2}$	71954·00	71958·5
$3s^23p^5$	$^2P_{1/2}$	881	882·5
	$^2P_{3/2}$	0	0

Many of the ionization potentials of chlorine are known. The table below is taken from Moore,[46] with the exception of the values in parentheses, which have been derived by Finkelnburg[65] by extrapolation.

TABLE I. - IONIZATION POTENTIALS OF CHLORINE

Initial State	Ionization potential	Initial State	Ionization potential
Cl I $3p^5\ {}^2P_{1/2}$	13·01 e.V.	Cl IX $2p^5\ {}^2P_{3/2}$	400·7 e.V.
Cl II $3p^4\ {}^3P_2$	23·80	Cl X $2p^4\ {}^3P_2$	455·3
Cl III $3p^3\ {}^4S_{3/2}$	39·90	Cl XI $2p^3\ {}^4S_{3/2}$	(531·4)
Cl IV $3p^2\ {}^3P_0$	53·5	Cl XII $2p^2\ {}^3P_0$	(594·0)
Cl V $3p\ {}^2P_{1/2}$	67·80	Cl XIII $2p\ {}^2P_{1/2}$	(656·6)
Cl VI $3s^2\ {}^1S_0$	96·7	Cl XIV $2s^2\ {}^1S_0$	(749·6)
Cl VII $3s\ {}^2S_{1/2}$	114·27	Cl XV $2s\ {}^2S_{1/2}$	(808·2)
Cl VIII $2p^6\ {}^1S_0$	348·3 ± 0·1		

The wave-length tables of the M.I.T.[66] list the following as the strongest lines of chlorine in the wave-length range 2000 to 10000A.:-

Wave-length, A.	Excitation potential, V.
4794·54	28·3
4810·06	28·3
4819·46	28·3

They arise from Cl II. The *raies ultimes* were investigated by de la Roche:[67] the excitation of lines of Cl in arcs has been noted.[68] The spectrum of HgCl has been used to determine the relative amounts of the chlorine isotopes in enriched samples.[69]

Wave functions for the chlorine atom[70,76] and for the chloride ion, Cl^-,[70-72,76] have been calculated: the subject is reviewed by Hartree.[73]

Intervals in chlorine multiplets have been considered by Bechert,[74] and Watari[75] has used self-consistent Hartree functions to calculate the interval ${}^2P_{1/2}$ - ${}^2P_{3/2}$ in the ground state of Cl I: depending on the choice of screening constant, he obtains for the interval -649, -796, -778 $\mathrm{cm.}^{-1}$ as compared with the experimental value, -881 $\mathrm{cm.}^{-1}$

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X-Ray Spectra.

Measurements of the *K* lines of chlorine have been made by a number of workers.[1-10] The wave-length shows some dependence on the source: thus

Lundquist[9] gives the following wave-lengths for K_{α_1} and K_{α_2}.

Source	K_{α_1}	K_{α_2}
Chlorides: Li^+, Na^+, K^+, Ca^{++}, Sr^{++}, Ba^{++}, Cu^{++}, Zn^{++}, Cd^{++}, Fe^{+++}	4718·33 X.U.	4721·29 X.U.
Chlorates: Na^+, K^+	4716·15	4719·10
Perchlorates: Na^+, K^+	4715·38	4718·38

K_α satellite lines have been studied by Stensson,[1] Dolejšek,[3] and by Parratt,[11,12] who has also measured relative intensities. The origin of the K_α satellites has been discussed.[13,14] The wave-lengths of the K_β lines[2,4,5] also depend on the source: for example, the line K_{β_1} appears with two components K_{β_1} at 4394·2, K_β'' at 4390·6 X.U. as excited from sodium chloride, several other chlorides and sodium and barium chlorates, but as a single broad line K_{β_1}'' at 4393·3 X.U. from lithium chloride and several other chlorides.[7] These effects have been confirmed[15,16] and discussed in relation to the electronic energy bands in the crystals.[17] Some of the weak lines appear to arise from transitions of valence electrons belonging to one of the ions into a vacancy in the K-shell of the other ion.

The K absorption band of chlorine has been much studied. The structure of its edge is often complex[18] and its position is somewhat dependent on the source.[19,20] The wave-length shifts of the edge have been studied in a wide variety of chlorine-containing compounds.[21-26,30,34,35] The ways in which the environment of the chlorine atom or ion may produce these shifts is discussed, for example by Pauling.[27] The relation of the energy difference between K absorption and emission is considered in relation to the ultra-violet absorption bands of the crystal by Das Gupta.[28,29] The fine structure of the K edge[30,31] varies from compound to compound.[32-35] A theoretical treatment has been given by Kronig[36] (see also Petersen[37]), who considers that the structure arises through transitions of K electrons into the energy bands in the absorbing crystals. According to this view, the structure of the edge is bound up with the electronic arrangement in the crystal and, as might be expected, detailed agreement with theoretical prediction is lacking;[38] some of the approximations involved in making numerical comparison between theory and experiment are serious.[39] The effects are not confined to solid absorbers, for the K-structures in gaseous chlorine and hydrochloric acid are complex and differ one from another[34,57] (see page 776). Emission lines appearing at the upper and lower limits of absorption edges are discussed by Satô.[40]

Absorption coefficients at wave-lengths below the K region have been measured.[41-43] The results of Colvert[42] between 0·496 and 2·288A. are in good agreement with those of Hansen[43] who studied the range 0·162 to 1·933A. The values of Woernle[41] extend from 2 to 10A., *i.e.* above the K region, but appear to be less reliable. Values of the mass absorption coefficients have been calculated[44] from 0·064 to 2·50A.

The L series in chlorine has been studied by Mohler and Foote[45,46] by a critical potential method; they found limits at 62·5, 70·5, 78·6A. Levi[47] measured an L series potential corresponding to about 55A., and M at 507A. Siegbahn and Magnusson[48] made accurate spectrographic observations of the lines, and give the following wave-lengths; L_η at 67·25A., L_l at 67·84A. A number of other lines, dependent on the nature of the source, was also found.[56] Intervals in the X-ray spin-doublets of the L and M series have been calculated. [49]

The soft X-ray region has also been studied in absorption: the L_{III} limit for chlorine lies at 61·1A.;[50,51] structure in the L absorption band arising from the transition of an L electron to an optical level has been observed.[52]

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The calculation of absorption edges from optical and X-ray line data, and the application of the regular doublet law have been considered.[53] Tables have been published[54] giving empirical mass absorption coefficients for wavelengths below the K limit and between the L_{I} and M_{I} limits. The efficiency of fluorescence of K-radiation from chlorine has been determined.[55]

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THE CHLORINE MOLECULE

The absorption spectrum of chlorine has attracted much study. It consists of a series of bands, sharply degraded to longer wave-lengths, which have been observed from about 5800A. to a convergence limit at about 4785A; at shorter wave-lengths there is continuous absorption, with $\lambda_{max} \simeq 3300$A.[1-5] Following several sets of measurements,[4-6] the correct vibrational analysis of the band-system was given[7,8] from a study of the vibrational isotope effect. A complete list of bands is given by Weizel.[9] The system is very weak, so that for observation of the outlying bands at the long wave-length end of the system, a path of 33·6 metres at 2 atmospheres was used.[10] The structure of several bands has been analysed by Elliott,[11] who found that the bands of a given isotopic species consist of single P and R branches. Shrader[12] has analysed one of the bands of $(^{37}Cl)_2$, using an isotopically enriched sample. Mulliken[13] showed that the transition is $^3\Pi_{0_u^+}$ (0_u^+) - $^1\Sigma_g^+$. Both Elliott and Shrader found values for the nuclear spin from the difficult measurement of the relative intensities of the band-lines, obtaining $i = 5/2$ for ^{35}Cl and ^{37}Cl respectively: it is now known, however, that the correct value for both isotopes is 3/2. The other constants derived from the analysis of the bands are in good agreement with the results of other work. Thus the value $\Delta G''_{1/2} = 556{\cdot}9$ cm.$^{-1}$ for the gas may be compared with the value 556 cm.$^{-1}$ obtained[14] from observation of the Raman shift in liquid chlorine. Similar concordance is shown by the figures which have been obtained for the internuclear distance:-

State	Method	r'' (A.)	Reference
Gas	Band spectrum	1·995 (r''_0)	11
Gas	X-ray diffraction	2·0	15,16
Gas	Electron diffraction	2·01	17
Liquid	X-ray diffraction	2·01	18

The circumstance that the potential curve for the shallow upper state, 0_u^+, (for which $r_e = 2{\cdot}47_6$A.) happens to be so disposed with respect to that of the ground state that the observable transitions in absorption lead, as the wave-length decreases, first to bands of higher vibrational quantum numbers in the upper state, and finally to continuous absorption, makes possible the determination of a very reliable value of the dissociation limit.[4,19-21] The point where the energy difference between successive bands, $[(v'+1\,,0) - (v',0)]$, falls to zero gives the energy required for the dissociation of a molecule in the state 0_u^+ above the energy of $v'' = 0$ in $^1\Sigma_g^+$. The atomic products at this limit are[13,19] Cl($^2P_{3/2}$) + Cl($^2P_{1/2}$), so that the energy of dissociation of the molecule is obtained by subtracting the atomic energy of excitation of Cl($^2P_{1/2}$) from the energy corresponding to the limit. Thus calculated,[22] $D''_0(Cl_2) = 57{\cdot}08$ kg.-cal.

The variation of extinction coefficient with wave-length in the visible and ultra-violet absorption spectrum of chlorine has been examined in some detail. von Halban and Siedentopf[23,24] made a few accurate observations of the absorption at room temperature, but their results at the longer wave-lengths are incorrect, and no absorption can be detected[10] between 6000 and 11500A. Mrozowski[25] examined the absorption of the mercury line 5461A. Studies of the absorption in strongly dried chlorine indicate, reasonably enough, that the convergence limit is unchanged by drying the gas.[26] Measurements[27] in the region 5040 to 5320A. and a wide series of observations[28] in the range 2660 to 4250A. at several temperatures between 18° and 765°C. have been reported; the region between 4020 and 5430A. has also been studied[29] at temperatures between 18° and 709°C.

The theoretical analysis of the variation of the intensity of the continuous absorption with wave-length is capable of yielding important information about

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the transition and about the potential energy curve for the upper repulsive state. If it is assumed that the Franck–Condon principle holds, then the intensity of a transition in absorption is proportional to $\nu[\int\psi_{\nu'}.\psi_{\nu''}.dr]^2$, where $\psi_{v'}$ and $\psi_{v''}$ are the vibrational wave-functions for the upper and lower states. Quite simple assumptions have been used with success. For example, the upper potential curve may be represented by a straight line (at least over small ranges of r) and $\psi_{v'}$ by a so-called δ-function different from zero only at the classical turning-point: the function $\psi_{v''}^2$ has then simply to be reflected at the upper potential curve and finally to be multiplied by ν in order to obtain the desired intensity distribution.[30] The effect of temperature is to change the populations in the lower vibrational states in a known way,[31,32] and thus its study facilitates the analysis.[33-35] However, if the simple reflexion method is adequate, the variation with temperature may be calculated from the expression:-[36]

$$\epsilon_T(\nu) = \epsilon_0^{max}\ [\mathrm{Tanh}\ (\frac{\theta}{2T})]^{\frac{1}{2}}\ \exp - [\mathrm{Tanh}\ (\frac{\theta}{2T})](\frac{\nu-\nu_0}{\Delta\nu_0^*})$$

In this, $\theta = 1{\cdot}439\omega_0$, where ω_0 is the vibration frequency for the lower state in cm.$^{-1}$

ν_0 is the frequency corresponding to the absorption maximum.

$\Delta\nu_0^*$ is the half-width of the absorption curve at 0°K., and

ϵ_0^{max} is the extinction coefficient at the maximum at 0°K.

The temperature variation for ϵ^{max} is given simply by:-

$$\epsilon_T^{max} = \epsilon_0^{max}\ [\mathrm{Tanh}\ (\frac{\theta}{2T})]^{\frac{1}{2}}.$$

A comparison of calculated and experimental values of ϵ is given[16] in Fig. 1. It will be seen that the calculated values reproduce the observed trends rather well: it does not follow, however, that the assumptions made in this simplified treatment are justified, for the dipole strength certainly varies with internuclear distance. Fortunately, the effect on the intensity distribution of this variation seems likely to be small.[37]

Theoretical treatments of the distribution of intensity in the chlorine continuum have been given.[29,33-35,36] Aickin and Bayliss[29] were able to resolve the continuum into two components, *A* and *B*, with the following characteristics:

	Transition	ϵ_{max}	λ_{max}
A	${}^1\Pi_u \leftarrow {}^1\Sigma_g^+$	66	3300 A.
B	${}^3\Pi_{1u} \leftarrow {}^1\Sigma_g^+$ ${}^3\Pi_{0_u^+} \leftarrow {}^1\Sigma_g^+$	~1	4250 A.

The upper state ${}^3\Pi_{0_u^+}$ of the *B* complex is the upper state of the transition giving banded absorption at $\lambda > 4785$ A. The states ${}^1\Pi_u$ and ${}^3\Pi_{1_u}$ dissociate to give $Cl({}^2P_{3/2}) + Cl({}^2P_{3/2})$, whereas ${}^3\Pi_{0_u^+}$ gives $Cl({}^2P_{3/2}) + Cl({}^2P_{1/2})$ on dissociation.

Below the *A* continuum, which has been followed down to about 2500A., there lies a further absorption continuum in the Schumann region. The observations[38] extend as far as 1560A.: the value of λ_{max} is not known, nor have extinction coefficients in this continuum been measured.

When gaseous chlorine is excited in a discharge tube, there may be obtained, according to the conditions, bands of the $A\ {}^3\Pi_{0^+} - X\ {}^1\Sigma^+$ system, a number of continua or quasi-continua especially in the ultra-violet region at $\lambda \leqslant 3065$A., or bands attributed to the molecule-ion, Cl_2^+ (see page 632). Thus von Angerer[39] observed a continuum with a long wave-length limit at about 3180 A., and bands with $\lambda_{max} \approx 3200$, 2650A. were obtained by Ludlam and West.[40] Bloch and Bloch[41] examined a fluorescence spectrum. Continua emitted in the hydrogen–chlorine flame[42,43] have been ascribed to a recombination process:-

$$Cl + Cl^* = Cl_2 + h\nu.$$

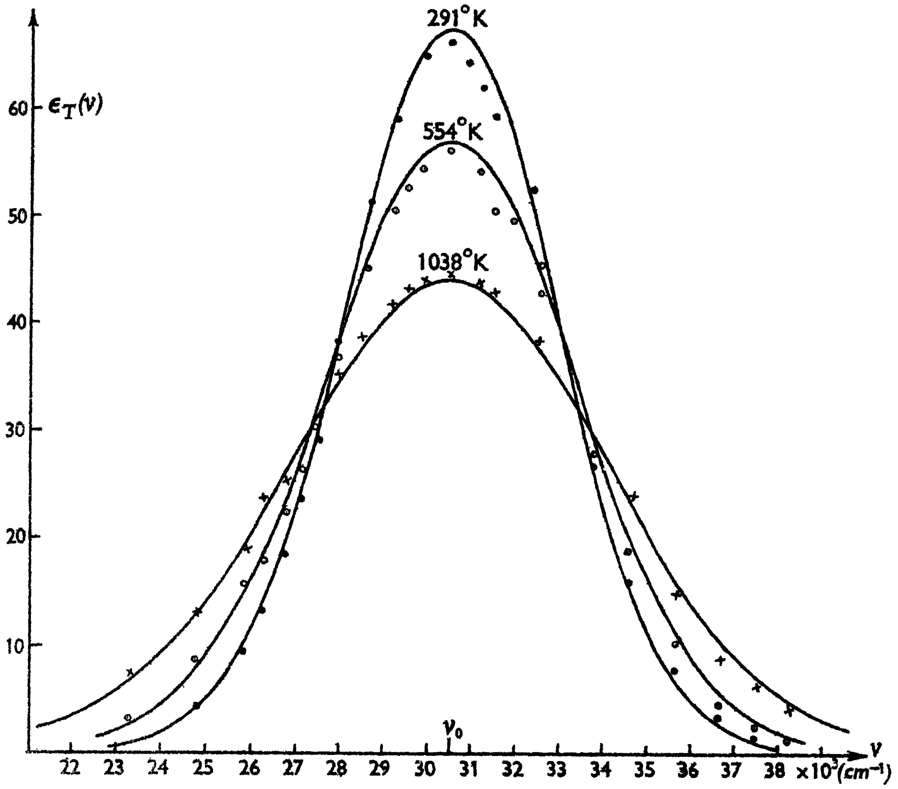

Fig. 1. THE ABSORPTION SPECTRUM OF GASEOUS CHLORINE AT DIFFERENT TEMPERATURES
THE POINTS ARE FROM THE MEASUREMENTS OF GIBSON AND BAYLISS:[28] THE CURVES ARE CALCULATED BY SULZER AND WIELAND.[36]

The flame also emits bands of the A – X system:[44] the system and the recombination continuum also appear in emission from heated chlorine[45-47] and from the photodissociation of lead chloride vapour.[48]

Earlier views[39,49] about the origins of the 2580 and 3065 A. continua are incorrect.[50,51] Elliott and Cameron[52,53] made the significant observation that the 2580 A. band, as excited in active nitrogen,[54] shows discrete vibrational structure with intervals around 220 to 250 cm.$^{-1}$ Thus this 'continuum' is certainly not, as was at one time suggested, an electron affinity spectrum, $Cl + e^- = Cl^- + h\nu$. The intensity of the 2580 system relative to that of the other ultra-violet continua is much increased in active nitrogen as compared with the intensities in the electrodeless discharge, suggesting that the initial states are different. Later measurements[55] of the emission 'continua' in the region 1835 to 3065 A. lead to their attribution[56] to transitions from three stable upper states of the chlorine molecule to repulsive or nearly repulsive lower states. This fits with Cameron and Elliotts' views[53] about the nature of the 2580 transition, although their detailed interpretations differ. Venkateswarlu's upper states are:-

$(\sigma_g)(\pi_u)^4(\pi_g)^3(\sigma_u)^2$ $1_g\ (^1\Pi_g)$ $T_0 \sim 75000$ cm.$^{-1}$
$(\sigma_g)(\pi_u)^4(\pi_g)^3(\sigma_u)^2$ $1_g\ (^3\Pi_{1g})$ $T_0 \sim 67700$
$(\sigma_g)(\pi_u)^4(\pi_g)^4(\sigma_u)$ $1_u\ (^3\Sigma_u^+)$ $T_0 \sim 58000$

It seems doubtful if this scheme is correct in all particulars, and further experimental work is clearly required.

The constants for the states of the chlorine molecule, $^{35}Cl_2$, are collected in Table II.

TABLE II. - SPECTROSCOPIC CONSTANTS FOR THE MOLECULE $^{35}Cl_2$

State	T_0	ω_e	$x_e\omega_e$	r_e
E ($^1\Pi_g$)	($\sim$ 75000)		stable	
D ($^3\Pi_{1g}$)	($\sim$ 67700)		stable	
	$\nu_{max} \geqslant 64100$		unstable	
C ($^3\Sigma_u^+$)	($\sim$ 58000)		stable	
$^1\Pi_u$	$\nu_{max} \sim 30300$		unstable	
$^3\Pi_{1u}$ A $^3\Pi_{0^+u}$	$\nu_{max} \sim 23525$		unstable	
A $^3\Pi_{0^+u}$	18147·4	239·4	5·42	2·476
X $^1\Sigma_g^+$	0	564·9	4·0	1·988

The absorption spectrum of crystalline chlorine at liquid nitrogen temperatures has been studied[57] at $\lambda \geqslant 2100$ A. The main absorption band occurs at 4900 to 5100 A., but there is further continuous absorption in the ultra-violet region. The pure quadrupole spectrum of solid chlorine at the same temperature has also been observed.[58,59] It consists of a single line at 54·248 Mc. ($^{35}Cl_2$): eQq is then (–)108·5 Mc. The value for the free atom is –110·4 Mc., and it therefore appears that the bond in the molecule uses essentially a p-orbital, with little, if any, s-hybridization (see page 633).

The absorption spectrum of chlorine dissolved in carbon tetrachloride is much like that of the gas: Gillam and Morton[60] found $\lambda_{max} = 3320$ A., $\epsilon_{max} = 99$. Even solution in water produces no change in the spectrum in the region 3500 to 4200 A., although at shorter wave-lengths the absorption increases to a maximum[61,73] below 2700 A. The character of the absorption does change, however, if chlorine is dissolved in benzene or *m*-xylene:[62] the maximum shifts to about 2900 A., and the results have been interpreted by assuming the formation of a 1:1 complex. Values of K given by $[Cl_2][Ar]/[Cl_2{:}Ar]$ at 25°C. and of ϵ for the complex are as follows:-

Solvent	$\epsilon_{complex}$	K
Benzene	9090	0·33
m-Xylene	6340	0·62

Reference has been made to some of the large body of work by Mulliken[13,68] on the interpretation of the spectrum of the chlorine molecule. He has considered the electronic arrangements in some detail, has predicted the existence of a number of states at high energies and has estimated ionization potentials.[63] The results of calculations of the absolute intensity of the transition in the long wave-length absorption band are in close agreement with the observed values.[37] Mulliken[64] has also given an interpretation of the high-intensity ultra-violet absorption spectra of the complexes formed between the halogens and derivatives of benzene. It is clear that theory has outstripped direct observation, and that more experimental work, especially in the Schumann region, is required.

The potential energy curve for the ground-state of chlorine deviates very little from the Morse curve,[65] but the Morse function gives only a poor representation of the state $A^3\Pi_{0_u^+}$.[29] Relations between energy of dissociation, force-constant and internuclear distance have also been considered.[66,67]

Thermodynamic properties of chlorine gas have been evaluated:[69-72] the spectroscopic value for the entropy is in good agreement with the calorimetric value.

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THE CHLORINE MOLECULE ION, Cl_2^+

The emission spectrum of Cl_2^+ may be obtained by passing a discharge through a stream of chlorine gas. It consists[1-4,7] of a series of bands stretching from about 5100A. to longer wave-lengths, grouped in pairs separated by about 140 cm.^{-1} at intervals of about 300 cm.^{-1} The band heads are indefinite. The even multiplicity indicates that the emitter is an odd-electron molecule and strongly supports the identification of the emitter as Cl_2^+. The analysis leads to the following constants[3] for $(^{35}Cl_2)^+$:-

$$\omega_e'' = 645{\cdot}3\ \text{cm.}^{-1},\ x_e''\omega_e'' = 2{\cdot}9\ \text{cm.}^{-1},\ r_e'' = 1{\cdot}891\text{A.},\ r_e' = 2{\cdot}29\text{A.}$$

It is not, however, entirely satisfactory: according to Howell[5] the doublet-splitting (~A) expected in the lower state, $^2\Pi_i$, is about 600 cm.^{-1}, and the vibration frequencies are probably $\omega'' \sim 630$, $\omega' \sim 310\ \text{cm.}^{-1}$. The difficulties in the analysis arise through the near-equalities, $A \sim \omega''$, $\omega'' \sim 2\omega'$.

The energy of dissociation may be obtained from the cycle:-

$$D_0\,(Cl_2^+) = D_0\,(Cl_2) + I.P.\,(Cl) - I.P.\,(Cl_2);$$

with Mackay's value[6] for the ionization potential of chlorine, this gives:-

$$D_0\,(Cl_2^+) = 2{\cdot}23\ \text{ev. or } 51{\cdot}4\ \text{kg.-cal}$$

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BROMINE MONOCHLORIDE, BrCl

The non-additivity of the absorption spectra of mixtures of chlorine and bromine (especially when allowed to equilibrate under ultra-violet light) settled the controversy about the existence of bromine monochloride.[1] This is seen from the following figures[2] for the absorption maxima, for solutions in carbon tetrachloride:-

	λ_{max}	Molar extinction coefficient
Cl_2	3320A.	99
Br_2	4170	208
BrCl	3800	97

Refs. p. 634

Measurements of this kind have been used to determine the thermodynamic constants for the formation of bromine monochloride:[3] studies have been reported of the gaseous equilibrium,[4] and of the equilibrium in carbon tetrachloride solution,[5] giving $\lambda_{max} = 3700$A. Earlier work has been reviewed[6] and tables of thermodynamic properties and of equilibrium constants for temperatures between 298° and 2000°K. have been given.[7]

The details of the visible and ultra-violet absorption band-systems of the gas do not appear to have been much studied: measurements have been made, but they have not been published.[8] Proceeding to shorter wave-lengths, a second region of absorption is found with $\lambda_{max} = 2150$A. At still shorter wave-lengths, two band-systems have been found[8] in the Schumann region. The constants for these states are given below:-

State	T_0	ω_e	$x_e\omega_e$
D	61600	$\Delta G_{1/2} = 504$	
C	59362	519	2·9
B	46500	-	-
A	27000	-	-
X	0	$\Delta G_{1/2} = 430$	

The approximate value of the ground state vibration frequency has been confirmed by observations of the fundamental vibration band[21] at $439{\cdot}_5$ cm.$^{-1}$ and of a Raman shift[9] of 428 ± 2 cm.$^{-1}$ in carbon tetrachloride solution. The dissociation energy may be obtained from the standard heat of formation of the gaseous compound, and the heats of dissociation of gaseous chlorine and bromine. The values given in the National Bureau of Standards list[10] are, at 298·16°K.:-

$$Q_f\,(\text{BrCl}) = +\ 3{\cdot}51 \text{ kg.-cal.}$$
$$Q_f\,(\text{Cl}) = +29{\cdot}01$$
$$Q_f\,(\text{Br}) = +26{\cdot}71$$

Thus D_{298} (BrCl) = 52·21 kg.-cal., or $D_0 = 51{\cdot}5$ kg.-cal.

The rotational constants for the ground-state have been determined with great accuracy from lines in the micro-wave region.[11] The lines observed correspond to the transitions $J\ 1 \leftarrow 0$ for $v'' = 0$ and 1. The internuclear distance, r_e, was found to be $2{\cdot}138 \times 10^{-8}$ cm. Interpretation of the Stark effect leads to the value $0{\cdot}57 \pm 0{\cdot}02$D. for the dipole moment. From these observations, precise values of the mass-ratios $m\,(^{35}\text{Cl})/m\,(^{37}\text{Cl})$ and of $m(^{79}\text{Br})/m\,(^{81}\text{Br})$, and of the quadrupole coupling constants were also obtained.

The electric charge of a nucleus with spin greater than one-half is generally not spherically symmetric. The interaction of nuclear spin with molecular rotation may then lead to a splitting of the rotational levels called nuclear quadrupole hyperfine structure, The quantity measured, the nuclear quadrupole coupling constant, is equal to eQq, where e is the electronic charge, Q is the nuclear quadrupole moment, and q is written for $\partial^2V/\partial z^2$ where V is the potential of the electric field at the nucleus for which the coupling is measured, and z is the co-ordinate along the symmetry axis. The interest of these measurements is considerable and arises because of the possibility of evaluating q, if Q (constant for a given nucleus) may be measured independently, e.g. in atomic beam experiments. q is determined by the electronic structure near the nucleus in question and the effects of the nuclei and electrons from other atoms nearly cancel. Further, closed-shell and s electrons make no contribution to q, the contribution from three equally filled p orbitals is also zero, and the contributions from electrons in states other than p is usually negligible if there are 'unbalanced' p electrons present. The measurements may therefore be interpreted to give the number of unbalanced p electrons, thus throwing significant light on the chemical binding in the molecules concerned.[12] The following results[13] illustrate the findings:-

Number of unbalanced p electrons (molecular $eQq/[2 \times$ atomic $eQq]$)

Molecule	From Cl	Molecule	From Br
Cl_2 (solid)	0·99	Br_2 (solid)	0·99
BrCl (gas)	0·94	BrCl (gas)	1·14
ICl (gas)	0·75	-	-
NaCl (gas)	0·01	NaBr (gas)	0·01

A value of 1·0 would correspond to a pure $p-p$ bond: lower values could arise through (sp) hybridization or from a high degree of ionicity. It appears that in Cl_2, Br_2 and BrCl the bonding is predominantly $p-p$, whilst that in NaCl and NaBr is highly ionic. The figure for ICl can be interpreted by saying that the bond has 25% ionic character.

The arrangement of electrons in the excited states of bromine monochloride has been studied theoretically by Mulliken.[14-19] The excited states of the interhalogens XY are somewhat different from those of the halogens X_2 because of their lower symmetry. The upper states of bromine monochloride are formulated as follows:-

$$\begin{array}{l} \mathrm{D}\ ([\sigma^2\pi^4_{\mathrm{Cl}}\pi^3_{\mathrm{Br}},\ {}^2\Pi_{1/2}]\sigma^{x})\ 0,1 \\ \mathrm{C}\ ([\sigma^2\pi^4_{\mathrm{Cl}}\pi^3_{\mathrm{Br}},\ {}^2\Pi_{3/2}]\sigma^{x})\ 2,1 \\ \mathrm{B}\ \sigma^2\pi^3_{\mathrm{Cl}}\pi^4_{\mathrm{Br}}\sigma^*,\ {}^{1,3}\Pi \\ \mathrm{A}\ \sigma^2\pi^4_{\mathrm{Cl}}\pi^3_{\mathrm{Br}}\sigma^*,\ {}^{1,3}\Pi \end{array}$$

Thus states C,D are related to the ground-state of the ion Br^+Cl, with Ω-s ($J-J$ like) coupling between the Br^+Cl core and the σ^x excited electron: A and B arise by excitation of a π electron associated with the bromine atom and with the chlorine atom respectively. The predicted ionization potentials are 12·43 (π_{Br}) and 13·66 (π_{Cl}) ev. A calculation of the bond-moment in bromine monochloride has been made.[20] An account of the infra-red spectrum of bromine monochloride has been published,[21] too late for consideration here.

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IODINE MONOCHLORIDE, ICl

The spectrum of iodine monochloride has been much studied, both experimentally and theroetically. The main absorption in the visible region corresponds to a transition $A^3\Pi_1 \leftarrow X^1\Sigma^+$. A large number of bands has been assigned to this system[1-7] which has been followed from about 8800A. nearly to the convergence limit at about 5750A.: beyond this limit is continuous absorption, with a maximum at about 4700A. A rotational analysis of the system A - X has been carried out.[7] Bands of a weaker system, $B^3\Pi_{0^+} \leftarrow X^1\Sigma^+$ lie at wave-lengths below the convergence limit.[8,9] These bands end abruptly at $v' = 4$, and transitions to $v' = 4$ are diffuse. The state $A^3\Pi_1$ gives, on dissociation, ground state atoms $I(^2P_{3/2}) + Cl(^2P_{3/2})$: $B^3\Pi_{0^+}$ is formed from $I(^2P_{3/2}) + Cl(^2P_{1/2})$, and it is concluded[9,10] that the state B is predissociated by a state $B'0^+$ which arises from the ground-state atoms. The level $v' = 4$ lies at about 600 cm^{-1} above the level of dissociation into normal atoms, while the energy of excitation of $Cl(^2P_{1/2})$ above $Cl(^2P_{3/2})$ is 881 cm^{-1} Brown and Gibson[9] were able to resolve some rotational structure at energies above the predissociation point, which may be ascribed to a transition $B'0^+ \leftarrow X^1\Sigma^+$: however, not all the lines are sharp, and there is evidently considerable mixing of the levels B + B

At shorter wave-lengths, there is found a region of continuous absorption at about 2400A.:[11] extinction coefficients in this continuum were measured by Binder[12] at temperatures between 293 and 685°K. The wave-length of maximum absorption was found to be 2440A. The absorption followed Beer's law at the pressures studied. The upper state responsible for this continuum may perhaps be identified with $B'0^+$ Further band-systems in the Schumann region have been discovered in absorption.[11,13]

Little is known of the emission spectrum of iodine monochloride. Filippov[14] mentions briefly the spectrum emitted in presence of nitrogen, and Asundi and Venkateswarlu[15] have published a more detailed description of a discharge through the vapour of iodine monochloride. Some eight diffuse bands in the region 18750 to 27050 cm^{-1} are found: they are considered to arise from transitions from stable upper states to sets of repulsive lower states. Constants for the electronic states are collected in Table III.

TABLE III. - CONSTANTS FOR THE ELECTRONIC STATES OF IODINE MONOCHLORIDE

State	T_0	ω_e	$x_e\omega_e$	$y_e\omega_e$	r_e
D	58191	(430)	-	-	<2·321
C	53478	(430)	-	-	<2·321
-	41000	(continuum)		-	-
$B'\ 0^+$	17981	-	-	-	-
$B\ ^3\Pi_{0^+}$	17258	(242)	(13)	-	$2{\cdot}6_1$
$A\ ^3\Pi_1$	13658	209·75	$1{\cdot}947_4$	$-0{\cdot}0336_6$	$2{\cdot}707_2$
$X\ ^1\Sigma^+$	0	384·18	1·465	-	2·3207

Iodine monochloride was the first diatomic molecule whose pure rotation spectrum was investigated by the methods of micro-wave spectroscopy. Weidner[16] studied the transition $J\ 1 \leftarrow 0$, and subsequently corrected his results for the by no means inconsiderable nuclear quadrupole effects.[17] The transition $J\ 4 \leftarrow 3$ has been studied under high resolution.[18] It is a complex spectrum; what would be a single transition for the ground-state of a single isotopic species is here broken up into about 150 lines by nuclear quadrupole effects.[19] Fortunately most of the intensity is concentrated in a smaller number of lines, of which about 25 were measured. The values of the rotational constants are in excellent agreement with the results of the rotational analysis of the A - X system,[7] thus:-

	B_e $I^{35}Cl$	α_e
Electronic spectrum:	0·11414	0·000502 cm^{-1}
Micro-wave spectrum:	0·114162	0·000536

Refs. p. 636

The mass-ratio m (^{35}Cl)/m (^{37}Cl) was found to be 0·945980 ± 0·000005, in good agreement with the value 0·945977 ± 0·000004 deduced from the microwave-spectrum of chlorine monofluoride (see page 224). From intensity measurements, the dipole moment was found to be 0·65 ± 0·06D. The quadrupole coupling constants eQq were also evaluated: their significance has already been considered (see page 633).

The dissociation energy of iodine monochloride is found from the convergence limit in the system A – X, at 17365 cm.$^{-1}$ This limit corresponds to dissociation into normal atoms,[20,21] so that D_0'' = 17365 cm.$^{-1}$ or 49·64 kg.-cal.

As is the case with other halogen molecules, understanding of the electronic states of iodine monochloride has been greatly furthered by the theoretical studies of Mulliken (see page 634[14-19]). The states of iodine monochloride are analogous to those of bromine monochloride discussed above. The predicted (vertical) ionization potentials are 11·16 (π_I) and 13·66 ev. (π_{Cl}). No adequate treatment of the absolute intensities in the longer wave-length part of the spectrum of iodine monochloride can yet be given, for more transitions are expected than have yet been observed.

Computations of the bond-moment have been carried out,[22,23] and the relation between force-constant and polarizability has been considered.[24]

Measurements of the apparent extinction coefficient of iodine monochloride at 5615A. in presence of a foreign gas have been made.[25] The solutions in inert solvents such as carbon tetrachloride and chloroform are brown and their absorption spectra are similar to those of the vapour,[26,27] with $\lambda_{max} \sim$ 4600A. With oxygenated solvents, on the other hand, such as ether, ethyl acetate and acetic acid, solutions are yellow, with $\lambda_{max} \sim$ 3550A. The peak value of the extinction coefficient is little changed. Mulliken[28] considers that this behaviour indicates the formation between the monochloride and the oxygenated solvent of complexes having structures similar to those of the better-known iodine complexes, but more tightly bound, and near that of a normal valence compound of oxonium type. Evidence for the formation of 1:1 complexes with benzene and substituted derivatives has been put forward:[30] the complexes are characterized by a strong absorption band with $\lambda_{max} \sim$ 3000A. In the case of benzene, for example, ϵ_{max} = 9900, and the equilibrium constant, $[ICl][C_6H_6]/[ICl.C_6H_6]$ has the value 4·76 at 25°C.

Solutions of iodine monochloride in aqueous hydrochloric acid or sodium chloride show a new absorption band at 3420A.[27] with an extinction coefficient greater than is found in the other solutions.

Thermodynamic properties, and the constants for the dissociation of iodine monochloride have been tabulated over the range 298 to 2000°K.[29]

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HYDROGEN CHLORIDE

Rotation Spectrum.

The infra-red spectra of the gaseous hydrogen halides played a most important part in the development of the spectroscopy of diatomic molecules:[1-10] for a summary, see, for example, Jevons.[11] The first measurements of a pure rotation spectrum were made[12,13] on hydrogen chloride in absorption by means of a grating instrument. A residual-ray technique was later used[14] and more recently lines in the extreme infra-red have been measured,[15] and accurate observations[16] have been made both on hydrogen chloride and on deuterium chloride. The spectrum has also been observed in emission,[17] using as source the flame of hydrogen burning in chlorine: here lines were observed not only from $v'' = 0$, the lowest vibrational level, but also from $v'' = 1$.

The rotational energy of a diatomic molecule may, with certain reservations, be written:-

$$F(J) = BJ(J+1) - DJ^2(J+1)^2 + \cdots, \quad J = 0,1,2 \cdots.$$

In the present case, the selection rule $\Delta J = \pm 1$ operates, so that the wave-number of the Jth line is:-

$$\begin{aligned} \nu(J) &= F(J+1) - F(J) \\ &= 2B(J+1) - 4D(J+1)^3 + \cdots \end{aligned}$$

where $B = h/8\pi^2 cI$, with I the moment of inertia, and $D \cong 4B^3/\omega^2$ is a constant expressing the centrifugal expansion of the molecule. Generally, $B \gg D$, so that the rotation spectrum consists of nearly equally spaced lines, $2B$ cm.$^{-1}$ apart.[18] Measurements of this spectrum are collected in Table IV. The calculated positions of the lines are from values of B and D determined from the vibration-rotation spectrum. They fit well with the observed positions up to $J = 10$, but the differences between observed and calculated values increase systematically at high values of J. This is no doubt due in part to the neglect of a term $+6H(J+1)^5$ in $\nu(J)$.

Measurements of the absolute intensity of absorption in this spectrum have been made,[19] and the line-widths have been studied.[55]

Vibration-rotation Spectrum.

The vibration-rotation spectrum of hydrogen chloride has been much studied: a review of the earlier work is given in Jevons' report.[10] The vibrational energy of a diatomic molecule may be written:-

$$G_v = \omega_e(v + \tfrac{1}{2}) - x_e\omega_e(v + \tfrac{1}{2})^2 + \cdots,$$

$v = 0,1,2 \cdots$, where ω_e is the vibration frequency and $x_e\omega_e$ is an anharmonic coefficient: $\omega_e \gg x_e\omega_e$. The fundamental absorption band corresponds to

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TABLE IV.- THE ROTATION SPECTRUM OF HYDROGEN CHLORIDE

Reference:	12,13,18	15	16	17	§	§
J	Values of ν, cm.$^{-1}$				$H^{35}Cl$	$H^{37}Cl$
0	-	20·8	-	-	20·88	20·85
1	-	41·6	-	-	41·75	41·69
2	-	62·5	-	-	62·60	62·50
3	83·03	83·1	83·32	-	83·40	83·28
4	104·1	-	104·13	-	104·16	104·01
5	124·30	-	124·73	-	124·85	124·67
6	145·03	-	145·37	-	145·47	145·25
7	165·51	-	165·89	-	166·00	165·75
8	185·86	-	186·23	-	186·42	186·15
9	206·38	-	206·60	-	206·74	206·44
10	226·50	-	226·86	-	226·92	226·59
11	-	-	-	-	246·97	246·61
12	-	-	-	-	266·87	266·48
13	-	-	-	-	286·60	286·19
14	-	-	-	-	306·16	305·70
15	-	-	-	-	325·52	325·05
16	-	-	-	345·6	344·68	344·18
17	-	-	-	364·6	363·64	363·10
18	-	-	-	384·2	382·35	381·80
19	-	-	-	403·4	400·84	400·25
20	-	-	-	422·1	419·06	418·46
21	-	-	-	440·1	437·03	436·39
22	-	-	-	458·3	454·71	454·05
23	-	-	-	474·4	472·11	471·43
24	-	-	-	494·3	489·20	488·49
25	-	-	-	511·2	505·97	505·24
26	-	-	-	527·7	522·42	521·67
27	-	-	-	542·9	538·52	537·75
28	-	-	-	561·1	554·28	553·47
29	-	-	-	576·4	569·66	568·85
30	-	-	-	589·6	584·67	583·83
31	-	-	-	609·4	599·28	598·43
32	-	-	-	623·4	613·49	612·62

§ Calculated, with constants from Mills, Thompson and Williams.[34]

the transition $(v = 1) \leftarrow (v = 0)$. Overtone bands, $2 \leftarrow 0$, $3 \leftarrow 0$ etc., may also be observed, although the intensity decreases rapidly as Δv increases. A vibration-rotation band is the totality of allowed rotational transitions (in the present case, $\Delta J = \pm 1$) associated with a given vibrational transition. The spectrum is somewhat more complicated than the pure rotation spectrum, for the change in the rotational constant B with v is not negligible, and we may write:-

$$B_v = B_e - \alpha(v + \tfrac{1}{2}).$$

The fundamental band of hydrogen chloride lies at about 3·5 μ. The rotational structure of this band has been resolved:[20] additional lines were measured later in the spectrum of the heated gas.[21,22] The first harmonic (2 - 0 band) was found[23] at about 1·76 μ. Higher harmonics lie at wave-lengths in the region of the infra-red accessible to photography, and may be studied with grating spectrographs of high resolving power. The 3 - 0 band,[24] 4 - 0 band[25-28] and 5 - 0 band[26-28] have been studied in this way. The isotope effect between $H^{35}Cl$ and $H^{37}Cl$, recognized in Imes' tracings of the fundamental by Loomis,[29] and later resolved in this band[30] and in the first overtone,[30,31] is clearly marked in the high-resolution work of Mills, Thompson and Williams.[34] Claims[32] to have discovered lines to be ascribed to an isotopic molecule $H^{39}Cl$ have not been substantiated.[31] Measurements of the fundamental band of DCl at 4·8 μ were used to determine the ratio of the atomic masses of deuterium to hydrogen.[33]

Values of some of the rotational and vibrational constants for $H^{35}Cl$ are collected in Table V, where they are compared with calculated values. The excellent agreement between the constants derived from measurements of the fundamental bands of hydrogen chloride and of deuterium chloride[35] is illustrated by the following values derived for the internuclear distance:-

Molecule	r_e'', A.
$H^{35}Cl$	$1{\cdot}274_4$
$H^{37}Cl$	$1{\cdot}274_4$
$D^{35}Cl$	$1{\cdot}2745_8$
$D^{37}Cl$	$1{\cdot}2746_2$

Some of the other constants are known less well, and more work on overtone bands is required.

The effect of temperature of the absorbing gas, which alters the appearance of the bands by shifting the molecular populations in the initial quantum levels, has been studied.[36,37]

With one exception,[17] the work described above relates to observations of the spectrum in absorption. The emission spectrum in the region 3000 to 6000 cm^{-1} has been studied:[38] the source was a chlorine-hydrogen flame, and, from measurements of relative intensities it was deduced that the rotational and vibrational temperatures in this source are around 2500°K. The question of the emissivity of hydrogen chloride in the infra-red region has been considered.[39,54]

TABLE V. - THE VIBRATION-ROTATION BANDS OF HYDROGEN CHLORIDE: CONSTANTS FOR $H^{35}Cl$

Band-origins, cm^{-1}

Reference: Band	27,30	24	27	28	34	*
1-0	2885·82	-	-	-	2866·01	2885·82
2-0	5667·98	-	-	-	-	5668·05
3-0	-	8347·20	-	-	-	8347·01
4-0	-	-	10923·11	10922·64	-	10923·05
5-0	-	-	13396·55	13395·20	-	13396·51

Values of B_v, cm^{-1}

Reference: v	27,30	24	27	28	34	§
0	-	-	-	10·4440	10·4422	10·442
1	10·136	-	-	-	10·1380	10·138
2	9·830	-	-	-	-	9·834
3	-	9·5343	-	-	-	9·530
4	-	-	9·232	9·2615	-	9·225
5	-	-	8·933	8·9462	-	8·921

* Calculated, with $G_v = 2989{\cdot}74\ (v + \tfrac{1}{2}) - 52{\cdot}05\ (v + \tfrac{1}{2})^2 + 0{\cdot}056\ (v + \tfrac{1}{2})^3$; Herzberg.[18]

§ Calculated, with $B_v = 10{\cdot}594_3 - 0{\cdot}3042\ (v + \tfrac{1}{2})$; Mills, Thompson and Williams.[34]

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The relative intensities of the vibration-rotation bands of the hydrogen halides were considered by Rosenthal.[40] The electric dipole moment $p(\xi)$ may be written:-

$$p(\xi) = p_e + p'_e.\xi + p''_e.\xi^2/2! + \cdots$$

with $p_e^{(n)} = (\partial^n p/\partial \xi^n)_{\xi=0}$ and $\xi = (r - r_e)/r_e$ where r is the internuclear separation. Taking only the first two terms in this Taylor series, Rosenthal obtained the following values for the ratios of the absorption coefficients, α, in the hydrogen chloride bands:-

$$\begin{aligned} \alpha_{2-0}/\alpha_{1-0} &= 1{\cdot}76 \times 10^{-2} \\ \alpha_{3-0}/\alpha_{1-0} &= 0{\cdot}628 \times 10^{-3} \\ \alpha_{4-0}/\alpha_{1-0} &= 0{\cdot}343 \times 10^{-4} \end{aligned}$$

However, Lindholm,[26] found that the intensity of the 4 - 0 band is only a few percent. of the value calculated in this way.

The relative intensities of lines in the fundamental band of hydrogen chloride have been measured.[41]

Measurements of the absolute intensity of vibration-rotation bands are of considerable importance because they lead to knowledge of the variation of dipole moment with internuclear separation.[42-48] The quantity determined experimentally is the apparent integrated absorption coefficient, α', given by:-

$$\alpha' = \frac{2{\cdot}303}{p.l} \int \log\left(\frac{T_{0\omega}}{T_\omega}\right) d\omega$$

where p is the partial pressure of absorbing gas,
l the length of optical path, and
$T_{0\omega}$, T_ω the apparent incident and transmitted intensities of radiation when the instrument is set at wave-number ω.

The true value, α', is given by the limit of α' as $p.l$ goes to zero, or by the limit of α' as the total pressure is increased to infinity. Corrections for gas imperfection may be necessary. The relation of α to quantities of theoretical interest has been considered by Crawford and Dinsmore.[48] They derive:-

$$\begin{aligned} \alpha\,(\text{fundamental}) &= \frac{4\pi^3 N}{3hcQ} \cdot \gamma^2 (p'_e)^2\, \omega_e (1 - 2x_e) \\ \alpha\,(\text{first overtone}) &= \frac{2\pi^3 N}{3hcQ} \cdot \gamma^4 (p'_e)^2 (\rho''_e + a_1)^2\, \omega_e (1 - 3x_e) \end{aligned}$$

where N is the number of molecules per unit volume per unit pressure at the temperature of experiment,
Q is the complete partition function,
$\gamma^2 = 2B_e/\omega_e$,
$p'_e = \epsilon r_e$, with ϵ the effective charge,
a_1 is the first mechanical anharmonicity constant, and
$\rho''_e = p''_e/p'_e$, p'_e, p''_e having their earlier significance.

Measurements of the absolute intensities of the fundamental and first overtone bands of hydrogen chloride have been made by a number of workers. The most recent are by Penner and Weber[49] whose results are summarized on page 641. The results of Rollefson and Rollefson and of Hammer are from measurements of refractive indices in the infra-red, which further provide values of the dipole moments:[51] for HCl, $p^0_0 = 1{\cdot}120 \pm 0{\cdot}012$, for DCl, $p^0_0 = 1{\cdot}145 \pm 0{\cdot}012$D, and lead to a negative value of $\partial p/\partial r$. However, the difference between the values of p^0_0 for HCl and DCl is not understood, and the sign of $\partial p/\partial r$ is probably positive.[56,57] The results of Bartholomé,[52] which are in

Reference	α_F	α_O
	cm^2 atm^{-1}	
Bourgin[43]	156	-
Dunham[46]	-	2·52
Rollefson and Rollefson[50]	173	-
Hammer[51]	158	-
Penner and Weber[49]	160 ± 30*	3·68 ± 0·30*

* at 297 ± 2°K.

marked disagreement with these values, have been criticized by Kemble.[52]

Penner and Weber thence derive:-

$$p(\xi) = p_e^0 \pm [1{\cdot}21 \times 10^{-18}\xi + (1{\cdot}96 \times 10^{-18}\xi^2 \text{ or } -0{\cdot}302 \times 10^{-18}\xi^2].$$

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Raman Effect.

The Raman effect in gaseous hydrogen chloride was first studied by Wood.[1-3] In later experiments, Wood and Dieke[4] were able to observe not only the *Q*-branch of the vibrational Raman effect, but also lines of the *S*-branches of the rotational effect, the theory of which was treated by Hill and Kemble.[5] The *Q*-branch was found at $2886{\cdot}_0$ cm^{-1} from the exciting line (Hg 4047A.), in good agreement with the value of ν_0 for the $1-0$ vibration-rotation band, 2886·01 cm^{-1} The rotational displacements are given in Table VI. It will be noted that the rotational Raman shifts do not correspond with the lines of the pure rotation spectrum (see Table IV).

TABLE VI. - ROTATIONAL RAMAN EFFECT IN GASEOUS HYDROGEN CHLORIDE

J	Stokes Lines	J	Anti-Stokes Lines	ν (calc.)	
				$H^{35}Cl$	$H^{37}Cl$
$2 \leftarrow 0$	-	-	-	62·64	62·55
$3 \leftarrow 1$	101·1 cm^{-1}	-	-	104·34	104·19
$4 \leftarrow 2$	142·7	$4 \rightarrow 2$	143·8	146·00	145·78
$5 \leftarrow 3$	187·5	$5 \rightarrow 3$	183·3	187·57	187·29
$6 \leftarrow 4$	229·4	$6 \rightarrow 4$	232·2	229·01	228·67
$7 \leftarrow 5$	271·0	-	-	270·32	269·93
$8 \leftarrow 6$	312·9	-	-	311·46	311·01
$9 \leftarrow 7$	353·0	-	-	352·42	351·90

The calculated shifts are with

$$|\Delta\nu| = F(J+2) - F(J) = (4B - 6D)(J + \tfrac{3}{2}) - 8D(J + \tfrac{3}{2})^3.$$

The influence of change of physical state on the infra-red and Raman spectra of hydrogen chloride has been the subject of several investigations, which have yielded most interesting results although it cannot be said that they have yet received a full explanation. As the pressure of hydrogen chloride gas is increased, the rotational lines in the vibration bands become more and more broadened, so that in the first overtone the lines almost disappear at 45 atm. At 78 atm., there is no trace of discrete structure, although the classical *P*,*R* doublet is still observable.[6] Daure[7] first showed that the Raman effect in liquid hydrogen chloride differs from that in the gas: the long-wave-length edge of the *Q*-branch shifts from 2886 cm^{-1} to 2800 cm^{-1}, the maximum from 2879 to 2770 cm^{-1} [8] Hettner[9] found that the infra-red maximum for the liquid at 160°K. lies at 2785 cm^{-1} The first overtone band of the liquid has little resemblance to the vibration-rotation doublet of the gas.[6] Up to about 20°C. the band consists of a single sharp asymmetric maximum whose position varies with temperature, thus:-

	liquid		gas
Temperature	-100°	55°C.	
Density	1·23	0·83 g./c.c.	
ν_{max}	5550	5620	$\nu_0 = 5668$ cm^{-1}

Above about 20°C. the asymmetry becomes less pronounced, and the maximum broader, and there appears in the absorption curve a point of inflexion near the gas minimum. Vodar *et al.*[10] have examined the spectrum of the liquid in the region of the second overtone, finding in addition to the main band at 8130 cm.$^{-1}$ (ν_0 = 8347 cm.$^{-1}$ in the gas) a much weaker band at about 7750 cm.$^{-1}$ The shift to lower frequencies might be explained as a solvent effect, but the shift is in fact smaller than is observed in inert solvents of the same dielectric constant.

The behaviour of crystalline hydrogen chloride is complicated by the transition at 98°K. The Raman spectrum at about 155°K. shows a single broad maximum at 2764 cm.$^{-1}$,[11] in good agreement with the single infra-red maximum at 2768 cm.$^{-1}$ observed[9] at 100°K. At 77°K., two frequencies are observed in the Raman spectrum, at 2709 and 2759 cm.$^{-1}$, the former being the stronger.[12] Hettner[9,13] found that at 43° and at 85°K. the infra-red maxima lie at 2708, 2747 cm.$^{-1}$ These results were substantially confirmed by Lee, Sutherland and Wu,[12] who measured the maxima at 77°K.: they found the frequencies to be 2701 and 2744 cm.$^{-1}$, and also showed that there is evidence for a third, minor, band at about 2777 cm.$^{-1}$ and further structure above and below the main absorption. The structure observed by Shearin[14] probably arises from water vapour. The third band was also observed by Hettner[9] for films deposited at $T \leqslant 30$°K., and in these circumstances the two main bands are replaced by one very asymmetric band. The infra-red absorption of deuterium chloride at 77°K. appears to differ markedly from that of hydrogen chloride at the same temperature:[12] there are now three strong absorption maxima, at 1965, 1982 and 1992 cm.$^{-1}$ (ν_0 = 2090 cm.$^{-1}$ in the gas). These three peaks are in fact characteristic of an HCl-DCl mixture.[23]

The frequency shift on going from the dilute gas to the condensed phases provides clear evidence that there is strong interaction between hydrogen chloride molecules in the latter: the two peaks in either spectrum are interpreted as arising from zig-zag hydrogen-bonded chains in the crystal, and the small shift between the infra-red and Raman spectra from the coupling of pairs of chains.[24] The spectra of dilute solutions of HCl in DCl have shown[25] that the angle between adjacent molecules is about 102°.

Quantitative studies of these interactions have been limited to examination of the effect of broadening of the lines in the pure rotation and in the vibration spectrum of the gas.[15-17] Bhagavantam[18] estimated empirically that rotational structure in the Raman effect would disappear at about 130 atm. Weber and Penner[19] have made transmission measurements on the fundamental and first overtone bands of hydrogen chloride: the transmission proves to be a non-linear function of the total pressure, so that the simple Lorentz treatment (see, for example, Margenau and Watson,[20]) is inapplicable. The theoretical problem of interaction in the compressed gas has been considered.[21] Lindholm[22] studied the line-widths in the 4 - 0 band and in the pure rotation spectrum. He found that the observed widths (at pressures of the order of 1 atmosphere) arise from van der Waals and from resonance interactions.

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Solutions.

The vibration spectra of hydrogen chloride solutions have also been studied. Williams[1] showed that the fundamental band was shifted to smaller frequencies when benzene, chlorobenzene, nitrobenzene and *m*-nitrotoluene were used as solvents, and found that the shifts increased with the dipole moment of the solvent. The absorption coefficient in benzene solution is greater than for gaseous hydrogen chloride.[2] Leberknight and Ord[3] investigated solutions in benzene, chlorobenzene and carbon tetrachloride and found, contrary to Williams, a large shift (110 cm^{-1}) to smaller frequencies in the case of benzene: the intensity decreases from benzene to carbon tetrachloride. A range of non-ionizing solvents was studied in the infra-red by West and Edwards,[4] and the Raman effects were examined by West and Arthur.[5] These authors correlated the frequency shifts, $\Delta\nu$, with the dielectric constant D of solvent according to the expression:-

$$\Delta\nu/\nu = C[(D - 1)/(2D + 1)]$$

where ν is the unperturbed frequency of the fundamental in the gas and C is a constant. Still bigger shifts to smaller frequencies are found for oxygenated solvents: thus in dioxan, diethyl ether and ethyl acetate, the fundamental is displaced[6] from 3·4 to 4 μ, suggesting hydrogen-bonding between solute and solvent. Examination of the absorption in similar solutions between 0·8 and 1·2 μ revealed that the spectra were little affected by temperature.[7]

In fully ionizing solvents, there is no feature that may be recognized as a vibration of the hydrogen chloride molecule: thus no Raman line attributable to the molecule appears in moderately concentrated aqueous solution,[8,9] although at concentrations above about 9N. a line at 2630 cm^{-1} has been reported.[10] However the classification of solvent type is not quite clear, for contrary to the infra-red observations,[6] it has been stated that the Raman spectra of concentrated solutions in diethyl ether show no hydrogen chloride vibration.[5]

The effect of dissolved hydrogen chloride on the infra-red absorption of water has been studied. Suhrmann and Breyer[11] found changes particularly in the bands at 0·98, 1·2 and 1·45 μ, Ganz[12,13] in the bands at 0·77 and 0·845 μ. Plyler and Barr found that aqueous solutions of a number of acids show absorption bands at 2·4 – 2·5 and 5·5 μ not given by water:[14,15] on changing to deuterium chloride dissolved in deuterium oxide, the 2·4 μ band shifts to 3·4 μ, but the absorption at 5·5 μ remains.[16] (See also page 792).

The absorption in aqueous solutions of hydrogen chloride has been studied[17] at a wave-length of 4 cm.

Refs. p. 645

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Ultra-violet Spectrum.

Regions of continuous emission have been observed in the spectra of discharge tubes containing hydrogen chloride[1-3] and in the spectrum of the hydrogen-chlorine flame.[4] Energetic interpretations of these continua have been suggested,[2-4] but the processes themselves are obscure, and it is not certain that the hydrogen chloride molecule is directly concerned with the production of the shorter-wave-length continua, for similar continua are obtained in chlorine alone.[5]

Gaseous hydrogen chloride is transparent throughout the visible region of the spectrum, but continuous absorption may be detected in the quartz ultra-violet. There have been several investigations of the absorption in this region, and also attempts to interpret the results in terms of the dissociation energy of the molecule:[6-9] however, since the upper potential curve for the repulsive state falls steeply[11] with increasing internuclear distance, it is clear that no reliable estimate of the dissociation energy can be obtained from measurements of this kind. The main part of the absorption band lies at wave-lengths below 2000A. This region was first studied by Leifson,[10] but it seems that his hydrogen chloride was impure, for his results were not confirmed by Romand,[11] whose values for the extinction coefficient fit well with those of Vodar[12] at longer wave-lengths (Fig. 2). The spectrum is that of a single broad band, with a maximum at about 1535A. From the variation in extinction coefficient with wave-length, Romand calculates the shape of the potential curve for the upper repulsive state between $r \sim 1{\cdot}1$A. and $r \sim 1{\cdot}8$A. The refractive indices of gaseous hydrogen and deuterium chlorides in the visible and ultra-violet regions down to 2300A. have been studied.[43]

At still shorter wave-lengths, Price[13] has found banded absorption, beginning at 1331A. The bands arise from transitions from the ground state X to two main states B,C whose constants are as follows:-

	$\nu_{0,0}$	ω_e	$x_e\omega_e$
State C ($^1\Pi$)	77480	2710	20
State B ($^1\Pi$)	75134	-	-

The bands of C−X are degraded to longer wave-lengths, whereas the B−X band is not obviously degraded in either direction. In addition, there are subsidiary bands lying at 200 to 300 cm^{-1} towards higher energies than the main bands. No Rydberg series has yet been observed for hydrogen chloride, but a comparison of the term-values with those for methyl chloride, having a

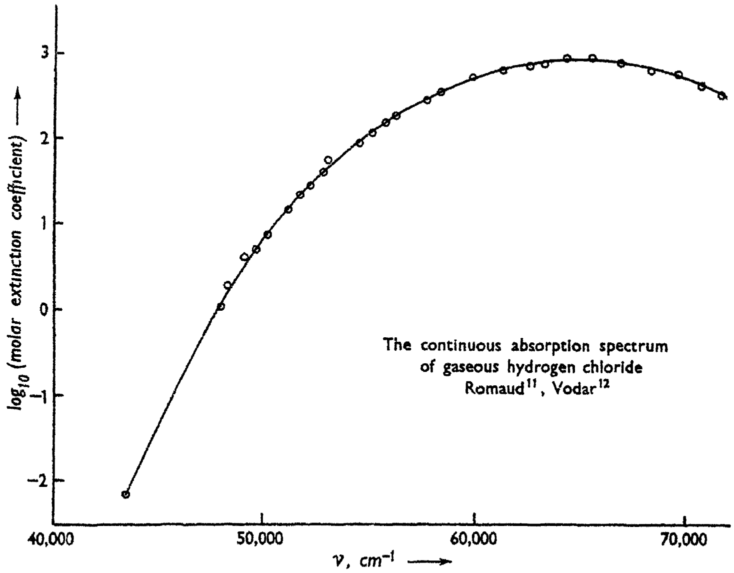

Fig. 2. THE CONTINUOUS ABSORPTION SPECTRUM OF GASEOUS HYDROGEN CHLORIDE (ROMAND;[11] VODAR[12])

spectrum closely similar to that of hydrogen chloride, leads to the value $12{\cdot}9_1$ ev. for the ionization potential of hydrogen chloride.[13,14]

The electronic states of the hydrogen halide molecules have been studied theoretically in great detail by Mulliken.[15,16] In earlier work,[17] he was able to predict a value, 13·66 ev., for the ionization potential of hydrogen chloride: subsequently he has derived an estimate of the absolute strength of the continuous absorption,[18,19] and has further correlated the experimental findings in the Schumann region with theoretical expectation.[20] The continuous absorption may be represented by:-

$$N\ \sigma^2\pi^4.\ {}^1\Sigma^+ \rightarrow Q\ \sigma^2\pi^3\sigma^*,\ {}^3\Pi,{}^1\Pi$$

and the states B and C as $B(\sigma^2\pi^3,\ {}^2\Pi_{3/2})b\sigma$, $C(\sigma^2\pi^3,\ {}^2\Pi_{1/2})b\sigma$: they are considered to be the first two members of two Rydberg series of states. No comparison between the experimental and theoretical values of the strength of the N → Q continuum appears yet to have been made.

The ionic-covalent resonance model has been used to discuss the bond moment[21] and the height of the first excited state above the ground state.[22] The potential energy function for the ground-state has been considered.[23,42] The relation of the force-constant in hydrogen chloride to that in other hydrides has been discussed,[24] and the relation between force-constant and internuclear distance has been examined.[25] Fajans[26] has considered the electron affinity of hydrogen chloride. Horváth has calculated the binding energy.[40]

Thermodynamic properties of gaseous hydrogen chloride have been calculated from the spectroscopic information[27-29,44] and a study of the isotopic effects has been made.[29] The value calculated for the standard entropy ($S^\circ_{298\cdot1}$), 44·66 ± 0·05, is in good agreement[30] with the calorimetric, Third Law, value 44·47 ± 0·15.

No accurate value for the dissociation energy of hydrogen chloride can be obtained directly from spectroscopic data.[31,41] It is best obtained from the heats of dissociation of hydrogen and chlorine, and the heat of formation of hydrogen chloride gas. Using the values given in the National Bureau of Standards list,[32] there is obtained D_0 (HCl) = 102·25 kg.-cal. (0°K.).

The absorption spectrum of liquid hydrogen chloride was studied by Tréhin and Vodar[33] in the quartz ultra-violet. they found that the extinction coefficients were greater than for aqueous solutions. Aqueous solutions of hydrogen chloride and of various metallic chlorides have been studied in the same region.[34-39]

A red colour appears in anhydrous samples of solid hydrogen chloride which have been frozen quickly with liquid nitrogen (see page 427).

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HYDROGEN CHLORIDE ION, HCl^+

Discharges through hydrogen chloride gas, or through hydrogen in presence of a small amount of chloride impurity give rise to a band-system in the region 2800 to 4000A., which arises[1,2] from the molecule HCl^+. Rotational analyses

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of this system have been made by Kulp[3-5] and by Norling[6,7] who also studied DCl^+. The splitting of the rotational levels of the ground state, $X\,^2\Pi_i$, constitutes a good example of Λ-type doubling.[8] The constants for the two known states of $(H^{35}Cl)^+$ are as follows (Herzberg[9]):-

State	T_0	ω_e	$x_e\omega_e$	$y_e\omega_e$	r_e
A $^2\Sigma^+$	28119·3	1605·79	39·58	+0·342	1·5139
X $^2\Pi_i$	0	2675·4	53·5	-	1·3153

The dissociation energy of the ion into the ground states of H and Cl^+ may be obtained from the cycle:-

$$D_0\,(HCl^+) = D_0\,(HCl) + I.P.\,(Cl) - I.P.\,(HCl).$$

Substituting previously given figures:-

$$\begin{aligned} D_0\,(HCl^+) &= 102{\cdot}25 + 300{\cdot}1 - 297{\cdot}7 \text{ kg.-cal.} \\ &= 104{\cdot}_{65} \text{ kg.-cal.} \end{aligned}$$

Thus although the internuclear distance and the vibration frequency are respectively bigger and smaller in the ion than in hydrogen chloride itself, indicating somewhat weaker binding, the energy of dissociation of the ion is very slightly greater than for the molecule. The determination of the energy of dissociation by extrapolation of vibrational levels is considered by Gaydon.[10] For the electronic structure of the ion, the reader is referred especially to the work of Mulliken cited under hydrogen chloride.

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THE OXIDES OF CHLORINE

CHLORINE MONOXIDE, ClO

The band-spectrum of ClO was probably first observed by Urey and Bates,[1] who reported diffuse bands in the region 3600 to 4350A. occurring in the spectrum of a hydrogen-chlorine flame containing oxygen. Improved spectrograms were obtained by Pannetier and Gaydon[2,3] from the flame of hydrogen burning in an atmosphere of oxygen containing a little chlorine. The emission bands have $v'' = 4$ to 14, $v' = 0$ to 4. ClO has been observed in absorption by Porter.[4,5] The strongest bands lie in the region 2635 to 3035A., and constitute a long $v'' = 0$ progression. Porter produced ClO by flash photolysis; the mechanism suggested[6] is:-

$$\begin{aligned} Cl + O_2 &= ClOO \\ Cl + ClOO &= 2ClO. \end{aligned}$$

Under these conditions, ClO has a half-life of a few milliseconds. Its decomposition to chlorine and oxygen was followed by observations on the absorption spectrum of ClO: an intermediate Cl_2O_2 may be involved.

The constants ($cm.^{-1}$) which represent both emission and absorption bands

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are:-

	ν_e	ω_e	$x_e\omega_e$
Upper state	31077	557	11*
Ground state	0	868	7·5

* $y_e\omega_e$ is not negligible

The nature of the transition is unknown: the ground state is expected to be $^2\Pi$, and Porter has observed some band-heads separated by about 200 cm^{-1} from the main heads, so that perhaps $|A' - A''| \sim 200$ cm^{-1} A quite short extrapolation of the upper state vibrational levels leads to a limit at 37930 cm^{-1} The probable products at this limit are Cl(^{2}P) + O(^{1}D), since the ground state levels extrapolate roughly to 24680 cm^{-1} Thus the upper state limit corresponds to $D_0'' = 63{\cdot}0$ or 60·5 kg.-cal. according as to whether the state of the chlorine atom on dissociation is $^2P_{3/2}$ or $^2P_{1/2}$. The result may be given as $D_0'' = 61{\cdot}8 \pm 1{\cdot}3$ kg.-cal. or D'' (298°K.) = 62·5 ± 1·3 kg.-cal.

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DICHLORINE MONOXIDE: Cl_2O

The visible and ultra-violet absorption spectrum of chlorine monoxide has been studied.[1,2] The absorption is purely continuous; a plot showing the variation of extinction coefficient with wave-number is given in Fig. 3. Finkelnburg *et al.*[2] suggest that the initiation of the continuum corresponds to the process:-

$$Cl_2O + h\nu = Cl + ClO \ldots\ldots\ldots\ldots (1)$$

Rollefson and Burton[3] point out that dissociation according to:-

$$Cl_2O + h\nu = Cl_2 + O \ldots\ldots\ldots\ldots (2)$$

may also be important. With Q_f (Cl_2O) = 18·2, D (ClO) = 62·5 kg.-cal.: the minimum energy for process (1) is 36·5 kg.-cal., for (2) 41·0 kg.-cal. The wave-lengths corresponding to these energies are 7840 and 6980 A. respectively. The dissociation of Cl_2O into ground-state atoms, 2Cl + O, requires 99·0 kg.-cal. Finkelnburg *et al.*[2] suggest that this is the process taking place at 2560 A. (112 kg.-cal.).

The infra-red spectrum of Cl_2O in the vibration-rotation region has been studied[4,5] and fundamental frequencies assigned.[6-8] Hedberg[8] gives the following values: $\nu_1 = 688$, $\nu_2 = (320)$, $\nu_3 = 969$ cm^{-1}, but notes that the magnitude of the bending frequency, ν_2, is somewhat uncertain as the band at 1245 cm^{-1} from which it is derived is overlapped by HOCl impurity. An illustration of the actual form of the normal vibrations has been given by Herzberg.[9]

The structure of Cl_2O has not yet been determined spectroscopically: electron diffraction studies have been made by Sutton and Brockway[10] and by Dunitz and Hedberg.[11] The latter derive:-

$$r(Cl-O) = 1{\cdot}701 \pm 0{\cdot}020\text{A.};\ \angle Cl-O-Cl = 110{\cdot}8 \pm 1^\circ.$$

Theoretical discussions of the structure of the molecule have been given.[12,13]

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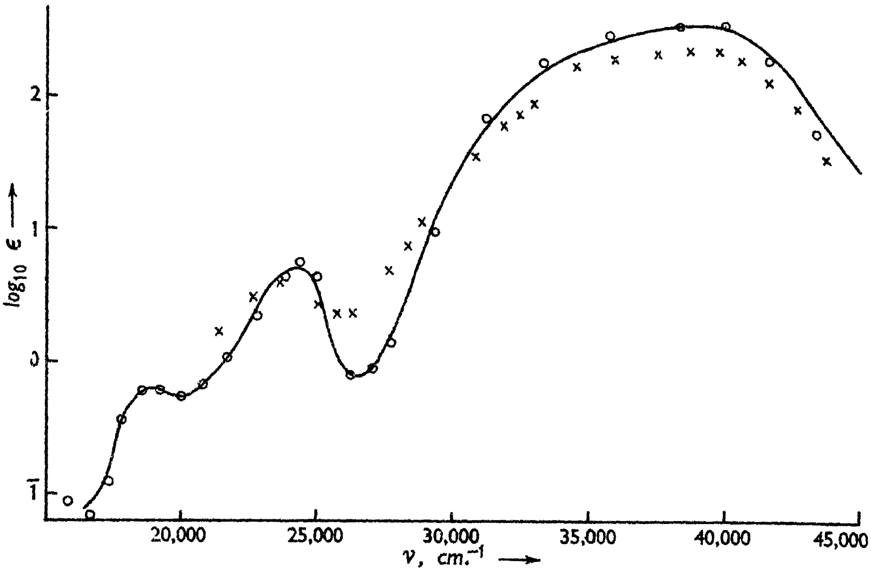

Fig. 3. THE ABSORPTION SPECTRUM OF CHLORINE MONOXIDE, Cl_2O.
x · · · GOODEVE AND WALLACE[1]
O · · · FINKELNBURG, SCHUMACHER AND STEIGER[2]

Yost and Felt[14] found the standard entropy of gaseous dichlorine monoxide to be 67·9 g.-cal. mole^{-1} degree^{-1}: the more reliable value, 63·7 ± 0·3, has been calculated from the molecular constants.[15]

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DICHLORINE TRIOXIDE: Cl_2O_3

Absorption bands observed by Kantzer[1] and attributed by him to a molecule Cl_2O_3 have been shown by Goodeve and Richardson[2] to arise from ClO_2. There

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is no spectroscopic evidence for Cl_2O_3.

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CHLORINE DIOXIDE, ClO_2

The absorption spectrum of chlorine dioxide in the region 2750 - 5250A. has been known for many years, and the vibrational analysis of this system has been studied by a number of workers.[1-5] The bands are degraded to longer wave-lengths: those at the shorter wave-length end of the system are predissociated so that bands at $\lambda < 3200$A. have only diffuse heads.[6] The observation of the onset of predissociation is determined partly by the resolving-power of the spectrograph employed: Goodeve and Stein[2] observed predissociation at $\lambda < 3293$A., Finkelnburg and Schumacher[6] at $\lambda < 3750$A., but Coon[7] found that the lines of the (6,0,0 - 0,0,0) band are broad (1 - 2 cm^{-1}), thus fixing the onset of predissociation at $\lambda \sim 3975$ A. At shorter wave-lengths, the bands become gradually weaker and more diffuse: their extrapolated point of disappearance[6] is 2563A. It is suggested[6] that the predissociation process is $ClO_2 \rightarrow ClO + O(^3P)$, and the process at the low wave-length limit is $ClO_2 \rightarrow ClO + O(^1D)$; the wave-lengths given above correspond to energies of 71·9 and 111·5 kg.-cal. $mole^{-1}$ respectively, in reasonable accord with the thermochemical values 60·1 and 105·5 kg.-cal. $mole^{-1}$ derived using $D''(ClO) = 62{\cdot}5$ kg.-cal.

The vibrational analysis of these bands leads[7] to the following values for $^{35}ClO_2$:-

Excited state: $\omega_1' = 722{\cdot}0$, $\omega_2' = 296{\cdot}1$, $\omega_3' = 804{\cdot}4$
Ground state: $\omega_1'' = 964{\cdot}8$, $\omega_2'' = 451{\cdot}8$, $\omega_3'' = 1127{\cdot}3$.

$\nu_e = 21369{\cdot}5$ cm^{-1}

The upper state frequency which appears[8] most strongly in the transition is ν_1'.

This band system of ClO_2 is one of the very few systems of non-linear polyatomic molecules whose rotational structure has, in part, been resolved and analysed. This work has been done by Coon[9] who has studied the bands $(v_1',0,0 - 0,0,0)$ with $v' = 0$ to 5. They are parallel-type bands ($\Delta K = 0$) of considerable complexity, with spin-doubling (since ClO_2 has an odd number of electrons), and showing both K- and L-structure (K is the quantum number associated with the component of angular momentum around the symmetry axis, L that associated with the total angular momentum, excluding nuclear spin. The theory of these transitions has been set out by Mulliken;[10] the structural patterns are illustrated by Metropolis[11]). The structure is such that each vibrational band falls into a series of sub-bands described by a value of K. The spectrum is further complicated by the chlorine isotope effect.

Coon was able to deduce the configuration of the excited state of ClO_2 in terms of an assumed structure for the ground state. With $r''(Cl - O) = 1{\cdot}53$A., $\angle''O - Cl - O = 109°$, $r'(Cl - O) = 1{\cdot}805$A., and $\angle' O - Cl - O = 92°$. More reliable values $r'' = 1{\cdot}49$A., $\angle'' = 118{\cdot}5°$, are now available for the ground state (see below): with these $r' \sim 1{\cdot}73$A., $\angle' \sim 110°$. Thus in the excited state, the bond distance is considerably greater, the bond-angle somewhat smaller, than in the ground state. That there is this large change in the configuration of the molecule on excitation could have been predicted, qualitatively, from the extent of the spectrum (Franck-Condon principle): it is in accord with the big drop in the values of the fundamental frequencies on

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excitation. The nature of the electronic transition in this system has been considered.[12]

The infra-red spectrum of ClO_2 in the vibration-rotation region has been studied by Bailey and Cassie,[13] by Hedberg[14] and by Nielsen and Woltz.[15] The latter give $\nu_1 = 943{\cdot}2$, $\nu_2 = 445$, $\nu_3 = 1110{\cdot}5$ cm.$^{-1}$, in good agreement with the values derived[7] from the analysis of the electronic spectrum. The assignment $\nu_1 = 943{\cdot}2$ cm.$^{-1}$ (with ν_1 the totally symmetric vibration) is confirmed by the observation of a Raman line at 935 ± 8 cm.$^{-1}$ from ClO_2 in solution.[16] Values of the anharmonic constants have also been derived.[7,15]

In the infra-red spectrum, there also appears a band at 290 cm.$^{-1}$ which could not be ascribed to an impurity:[15] it is suggested that this band arises from a polymer of ClO_2.

Rotational structure in the vibration-rotation region has been analysed by Nielsen and Woltz.[15] They derive the bond-distance, $r(Cl - O)$ as a function of the bond-angle, $\angle O - Cl - O$, but neither is uniquely determined. However, by combining their results with those from the electron-diffraction work of Dunitz and Hedberg,[17] they obtain $r(Cl - O) = 1{\cdot}49$ A., $\angle O - Cl - O = 118{\cdot}5°$. In agreement with the fact that the Cl - O bond is short, the analysis of the vibration potential function of ClO_2 by Duchesne and Nielsen[18] indicates that the Cl - O bond in ClO_2 is strong.

It has been reported that ClO_2 absorbs in the microwave region of the spectrum,[19] but no analysis appears yet to have been published.

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CHLORINE TRIOXIDE: DICHLORINE HEXOXIDE

Goodeve and Richardson[1] have shown that in the liquid state and in solution this oxide exists as Cl_2O_6; in the gaseous state as ClO_3.

The gaseous oxide absorbs continuously[2] from a threshold at about 3500A.: there is a maximum at about 2780A. ($\log_{10} \epsilon \sim 3{\cdot}1$) and a second broad maximum at $\lambda < 2170$A. (see Fig. 4). Liquid dichlorine hexoxide absorbs strongly from about 6000A. to shorter wave-lengths;[2] no evidence has been found for more than one band. The extinction coefficient (molar decadic) of the hexoxide dissolved in carbon tetrachloride is 2·4 at 5460A. for a 0·1 M-solution,[3] as compared with $\epsilon \sim 80$ for the pure liquid at the same wave-length. It is suggested that this effect arises from interactions between the hexoxide molecules in the pure liquid.

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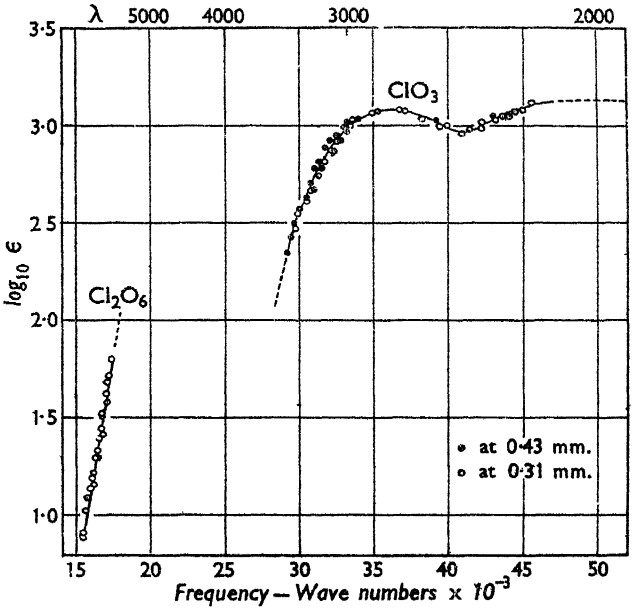

Fig. 4. ABSORPTION SPECTRUM OF CHLORINE TRIOXIDE

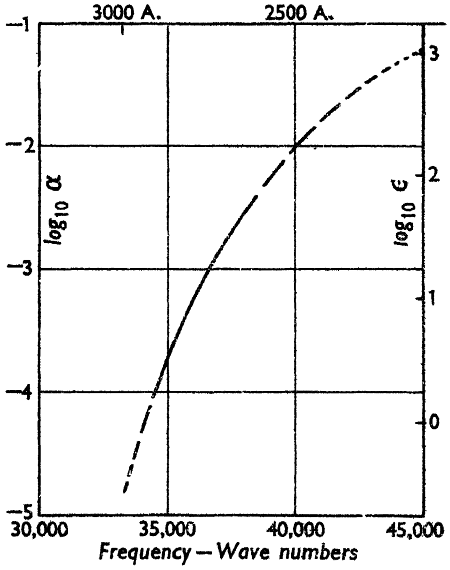

Fig. 5. ABSORPTION SPECTRUM OF CHLORINE HEPTOXIDE

DICHLORINE HEPTOXIDE, Cl_2O_7

The ultra-violet absorption by dichlorine heptoxide vapour has been studied.[1] The absorption is continuous, and the extinction coefficient rises smoothly from 3000 to 2000A., the low wave-length limit of the observations (see Fig. 5). Representative values are: at 34000 $cm.^{-1}$, $\log_{10} \epsilon = 0$; 45000 $cm.^{-1}$, $\log_{10} \epsilon = 3$.

The Raman spectrum of a 40% solution of dichlorine heptoxide in carbon tetrachloride was studied by Fonteyne,[2,3] who concluded that the spectrum contained lines characteristic of the ClO_3 group. This, together with the non-zero dipole moment (0·72 Debye), suggests a configuration $O_3Cl - O - ClO_3$ with $\angle Cl - O - Cl \neq 180°$.

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OXY-ACIDS OF CHLORINE

Hypochlorous acid: HClO.

The absorption spectrum of hypochlorous acid in aqueous solution has been studied in the ultra-violet region and the absorption in the vapour phase has also been examined: it is found that the extinction coefficients in the vapour are much higher than in solution.[1] The results for aqueous solutions have been confirmed.[2]

Chlorous acid: $HClO_2$.

Aqueous solutions of chlorous acid show considerable absorption between 2100 and 3000 A., with $800 > \epsilon > 50$; no maxima have been observed.

Chloric acid: $HClO_3$.

An examination of the Raman spectrum of a concentrated (40%) aqueous solution of chloric acid showed[3] that all the halogen is in the form of ions, ClO_3^-, of symmetry C_{3v}.

Perchloric acid: $HClO_4$.

Interesting information about the constitution of perchloric acid and its aqueous solutions has come from studies of the Raman effect.[4-11] Up to concentrations of about 70%, corresponding to $HClO_4,2{\cdot}4H_2O$, the spectrum is identical with that of the perchlorate ion, ClO_4^-, and shows the four fundamental frequencies expected for a tetrahedral structure (see, for example, Herzberg[12]) thus:-

	$\Delta\nu$,$cm.^{-1}$	Intensity	
ν_1 (symmetrical valence vibration)	930	20	polarized
ν_2 (2-fold degenerate deformation)	460	8	depolarized
ν_3 (3-fold degenerate valence vibration)	1120	1	depolarized
ν_4 (3-fold degenerate deformation)	625	8	depolarized

However, the spectrum of the anhydrous acid is different; the changes that occur on addition of water are illustrated by the figures[10] given in Table VII.

The anhydrous acid may be formulated $HOClO_3$, and appears to have[8,10] a pyramidal pseudo-acid structure of symmetry C_{3v}. Similar results have been reported for deuterium perchlorate.[9] Suggestions that acidium salts may be formed or that there may be association in aqueous solutions are not supported by the Raman spectra:[10] a discussion of these matters has been given.[13]

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TABLE VII. - RAMAN SPECTRUM OF PERCHLORIC ACID

Source:	$HClO_4$, 100%	89%	41%	$NaClO_4$, satd.
Raman shifts, cm^{-1}:	284	-	-	-
	424	429	-	-
	-	458	458	459
	577	577	-	-
	-	619	626	625
	740	750	-	-
	-	930	928	928
	1031B	1034B	995	-
	-	-	1120	1120
	1210B	1220B	-	-

B = broad line.

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CHLORIDE AND OXY-CHLORINE IONS IN SOLUTION AND IN THE SOLID STATE

The chloride ion, Cl^-.

The absorption spectrum of aqueous solutions containing the chloride ion has been studied at wave-lengths above 2000A. by a number of workers,[1-5] but the maximum of the absorption band apparently lies outside this range, at about 1810A.[6] The extinction coefficient at the maximum is high: $\epsilon \sim 10^4$. These intense ultra-violet absorption bands of the halide ions and of certain other anions are considered to arise from a charge-transfer process of the type:-

$$X^-(\text{solvent}) + h\nu \rightarrow X(\text{solvent}^-):$$

(for a review see Rabinowitch[7]). That it is possible to draw a consistent picture of the energy changes in this process can be seen, for example, from the following cycle used by Friedman.[8]

$$\begin{array}{ll}
X^-_{aq} + H^+_{aq} \xrightarrow{h\nu} X^* + e^{-*} + H^+_{aq} & N_0 h\nu \\
X^* + e^{-*} + H^+_{aq} \rightarrow X_{aq} + e^-_{aq} + H^+_{aq} & -\Delta H^* \\
X_{aq} + e^-_{aq} + H^+_{aq} \rightarrow X_g + e^-_g + H^+_g & \Delta H_s(e^-) + \Delta H_s(H^+) + \Delta H_s(X)
\end{array}$$

and:-

$$\begin{array}{ll}
X^-_{aq} + H^+_{aq} = \tfrac{1}{2}X_2(\text{standard state}) + \tfrac{1}{2}H_2(\text{standard state}) & -\Delta H^0_f(X^-_{aq}) \\
\tfrac{1}{2}X_2(\text{standard state}) + \tfrac{1}{2}H_2(\text{standard state}) = X_g + e^-_g + H^+_g & \Delta H^0_f(X_g) + \\
 & \Delta H^0_f(H^+_g)
\end{array}$$

so that:-

$$\Delta H_s(H^+) + \Delta H_s(e^-) - \Delta H^* = -N_0 h\nu - \Delta H_s(X) + \Delta H^0_f(X^-_{aq}) + \Delta H^0_f(X_g) + \Delta H^0_f(H^+_g) \quad ..(1)$$

The left-hand side of (1), (which corresponds to the sum of the heats of solvation of the proton and electron minus the heat of re-arrangement of the products of the absorption of one einstein of radiation) may be evaluated in a number of

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cases. Some of the values given by Friedman are listed in Table VIII.

If the identification of the transitions is correct, then variations in the sum of the terms on the right-hand side of equation (1) (last column of Table VIII) must arise from variations in ΔH^*. Now ΔH^* may be split into two terms,

TABLE VIII. - ENERGY TERMS IN THE CHARGE-TRANSFER SPECTRA OF SOME HALOGEN IONS, KG.-CAL.

Ion	$N_0 h\nu_{max}$	$-\Delta H_f^0(X_{aq}^-)$	$\Delta H_f^0(X_g)$	$\Delta H_s(X)$	$[\Delta H_s(H^+) + \Delta H_s(e^-) - \Delta H^*]$
Cl	158	40·0	29·0	2·7	275
Br^-	143	28·9	26·7	3·6	276
I^-	126	13·4	25·5	4·5	276
OCl^-	>150	25·9	25	3	<265
ClO_2^-	>150	17·2	24·7	7	<252
ClO_3^-	>150	23·5	37·0	7	<271

(i) arising from the re-arrangement of water molecules around X and around e^-, (ii) arising from changes in the structure within the radical X. In the case of the monatomic anions the latter term is zero, and it is found that here ΔH^* is constant. It is thus reasonable to attribute the spread in the values of ΔH^* for the polyatomic anions to changes in the structure between X_{aq}^- and X_{aq}. From the data for the monatomic ions it can be concluded that:-

$$\Delta H_s(e^-) + \Delta H_s(H^+) \geqslant 276 \text{ kg.-cal.}$$

The ultra-violet absorption spectrum of an aqueous solution of sodium chloride to which chlorine has been added differs from the spectrum of chlorine in water, and it is suggested that Cl_3^- ions are present.[9]

In the infra-red region, Ganz[10,11] has studied the effect of dissolved chlorides on the absorption bands of water at 0·77 and 0·845 μ.

Measurements of the absorption of aqueous solutions of chlorides at wave-lengths of 1·25, 3 and 10 cm. have thrown light on the dielectric properties of these solutions.[12,13]

The spectra of crystalline chlorides are considered under the appropriate, more electropositive, element.

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The hypochlorite ion, ClO^-.

The ultra-violet absorption spectrum of the hypochlorite ion in aqueous solution has been studied.[1,2] There is an absorption maximum at 2900A. ($\epsilon \sim 350$), and further strong absorption beginning at about 2200A. and extending to shorter wave-lengths. The latter is interpreted as a charge-transfer spectrum.[2]

The Raman spectrum of a saturated solution of sodium hypochlorite has been photographed, and a line at 713 ± 3 cm^{-1} has been attributed to the $(Cl - O)^-$ vibration.[3]

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The chlorite ion, ClO_2^-.

The absorption spectrum in the region 2000 to 4000A. of aqueous solutions containing the chlorite ion has been studied,[1] with results that do not confirm earlier work.[2] A basis for the theoretical interpretation of the absorption spectrum of the ion has been given by Mulliken[3] and by Walsh.[4] The short wave-length absorption, with $\lambda_{max} < 1900$A., is considered to be a charge-transfer spectrum.[1]

The Raman spectra of aqueous solutions have been investigated by Kujumzelis,[5] who observed a single shift at 802 cm.$^{-1}$, and by Mathieu,[6] who measured lines at 396 ± 5 cm.$^{-1}$ (m: polarized) and at 797 ± 5 cm.$^{-1}$ (strong: polarized). The third frequency expected for the non-linear ion has been observed in the infra-red[7] and Raman[6] spectra of crystalline sodium chlorite, $NaClO_2,3H_2O$, at about 844 cm.$^{-1}$ Mathieu's assignments for the frequencies of the ion are:-

ν_1 (symmetrical valence vibration): 797 cm.$^{-1}$
ν_2 (symmetrical deformation): 396
ν_3 (asymmetric valence vibration): 844

Mathieu's values for the Raman shifts in crystalline sodium chlorite are: 57 ± 3, 402 ± 3, 786 ± 2, 844 ± 2 and 1104 ± 3 cm.$^{-1}$ Duval, Lecomte and Morandat[7] observed the frequencies 860 and 1200 cm.$^{-1}$ in the infra-red spectrum of the powdered crystal: their assignments are however criticized by Mathieu.

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The chlorate ion, ClO_3^-.

The chlorate ion absorbs but little in the quartz ultra-violet region. Friedman's measurements[1] on the absorption spectrum of the ion in aqueous solution, using sodium chlorate, agree well with those of Farkas and Klein[2] in the range 2100 to 2300A. At lower wave-lengths there is some discrepancy: thus at 2000A. the former finds $\epsilon = 100$, the latter, $\epsilon = 65$. The maximum of the absorption band lies at some undetermined wave-length below 1900A.; the system probably arises from a charge-transfer process.[1,2]

The Raman spectra of aqueous solutions of chlorates have been studied by a number of workers.[3-7] The ion shows four frequencies: it is pyramidal, with the symmetry C_{3v}. The assignments of Shen *et al.*[5] are as follows:-

ν_1 . . . . 930 cm.$^{-1}$
ν_2 610
ν_3 982
ν_4 479

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Rolla[8] has studied the Raman spectra of several chlorates dissolved in ethyl alcohol and in acetone: the values of the frequencies attributed to the chlorate ion are but little changed from the values in aqueous solution (see also chloric acid, page 654).

The vibrational spectra of crystals differ from those of the 'free' ions in solution, for (i) the lattice vibrations may contribute to the crystal spectrum, and (ii) when the free ion is embedded in the crystal there is in general a lowering of symmetry which may lead to the splitting of degenerate frequencies and to the observation of frequencies which were inactive in the free ion (for a review, see Menzies[9]). A number of observations of the Raman effect in crystalline chlorates have been made;[4,10-18] the classification of the vibrations is considered especially by Couture and Mathieu.[16] Similarly, the infra-red spectra have been studied in some detail.[19-25] The ion retains its pyramidal structure in the crystal.

The spectral character of the iridescence of potassium chlorate crystals has been examined.[26,27]

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The perchlorate ion, ClO_4^-.

The perchlorate ion scarcely absorbs in the quartz ultra-violet region: thus Fromherz and Menschick[1] found $\epsilon \sim 0{\cdot}2$ at 2000 A. from observations on aqueous solutions of sodium perchlorate. Theoretical estimates of the positions of the lowest-lying electronic states of the perchlorate ion have been made.[2]

The Raman spectra of solutions of perchlorates have been studied.[3-7] The characteristic frequencies of the tetrahedral ion vary slightly with the cation, with concentration and with solvent,[5] but the effects are small. With silver perchlorate in toluene, however, a line appears at 167 cm.$^{-1}$ which has no counterpart in aqueous solutions of the silver salt, and the value of ν_1 drops from 929 cm.$^{-1}$ in water to 916 cm.$^{-1}$ in toluene:[6] the Raman shift at 167 cm.$^{-1}$

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also appears in a concentrated aqueous solution of mercuric perchlorate.[6] Hansen-Damaschun[7] has measured the relative intensities of the Raman lines from aqueous solutions of sodium perchlorate and has discussed these in terms of the type of valence bond obtaining in the ion.

The Raman spectra of crystalline perchlorates have also been examined.[3,8,9] The frequencies attributable to the ion are little changed from their values in solution: some of the details of the spectrum of crystalline lithium perchlorate, $LiClO_4,3H_2O$, however, are at present obscure.[9]

The infra-red spectrum of powdered potassium perchlorate has been examined.[10]

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SECTION XIX

THE ANALYTICAL DETERMINATION OF CHLORINE, CHLORIDE, HYPOCHLORITE, CHLORITE, CHLORATE, AND PERCHLORATE.

By L. A. HADDOCK

VOLUMETRIC ESTIMATION OF CHLORIDES USING INDICATORS

SEVERAL workers have studied the classical procedures of Mohr and Volhard for the determination of chloride ion. It has been shown[1] that the titration using potassium chromate as indicator must be carried out at pH 5 – 7, adding sodium acetate to reduce the acidity of solutions more acid than pH 5. Comparing the accuracy of the two methods it was found[2] that the Mohr method was highly accurate if the solution was quite neutral – pH 7. The Volhard titration of excess silver nitrate with potassium thiocyanate is ten times as sensitive, though appreciable quantities of potassium thiocyanate are liable to be adsorbed on the precipitated silver thiocyanate. Slavyanov[3] also described the procedures necessary to obtain accurate results by the two methods and it was shown[4] that the Volhard method would give results accurate to within 0·001 mg. of chlorine in 1 – 2 ml. of solution. The Volhard titration can be carried out without removing the precipitated silver chloride if 1 ml. of nitrobenzene is added for each 50 mg. of chlorine and the liquid is shaken in a stoppered bottle to coagulate the silver chloride before titrating with potassium thiocyanate in the usual way.[5]

A number of indicators other than ferric alum have been proposed for the Volhard method, mainly by Fajans and his collaborators. Dichlorofluorescein, having a larger ionization constant and absorbability, has advantages over fluorescein itself.[6] Diphenylamine blue, (oxidized $(C_6H_5)_2NH$), added to a solution in which the silver chloride is in the hydrosol form, causes the solution to appear green:[7] when precipitation is complete the adsorbed dyestuff is displaced by Ag^+ and the solution becomes clear and violet. By this method titrations can be made in solutions 5N. in acidity. The method can be used to determine Cl^- in presence of Br^- and I^-,[8] but an excess of indicator must be avoided.[9] The use of phenosafranine and tartrazine as adsorption indicators in the indirect titration of chloride has been described[10] as has the use of tartrazine instead of ferric ions as an indicator in the Volhard titration.[11] If dilute diphenylcarbazone solution is added[12] together with ether to a solution of chloride acidified with nitric acid the solution can be titrated with 0·1N-mercuric nitrate while stirring vigorously, the colour change being from yellow-brown to red. The same indicator has also been used[13] in titrating a solution of a chloride in presence of a mercuric salt and diphenylcarbazone in acetone with silver nitrate after addition of ether. The colour change in the ether is from pale brown to purple and then sharply to red-brown.

The Mohr method for chloride is normally carried out in neutral solution with potassium chromate as indicator. It can be made more sensitive by illuminating the solution from below with a 40 watt Osram K bulb and reflector or with light rich in the red end of the spectrum.[14]

Numerous organic compounds have been used as adsorption indicators in place of the chromate ion, e.g. fluorescein and its halogen substitution products.[15] It is said[16] that fluorescein derivatives give results more accurate than those obtained with chromate ions; these observations have been confirmed[17,18,19] and the use of metanil yellow and the sodium salt of bromophenol blue have been proposed. Fluorescein may serve to detect as little as 1 µg. of Cl^- or Br^-, alone or in presence of each other.[20] In the latter case bromine is first liberated by boiling the solution with lead dioxide and dilute acetic acid, and after adding sulphuric acid chlorine is subsequently distilled.

Iodine and chlorine are determined in admixture by the use of Brilliant Orsella C and chromatrope F.4C,[21] while sodium fluorescein, umbelliferone, β-methylumbelliferone, thioflavin S, erythrosin and primuline etc. have been used as indicators in the titration of chloride against silver nitrate in filtered ultraviolet light;[22] in this way Cl^- may be determined in presence of CNS^- and I^-. A mixture of fluorescein and methylene blue has also been used for titrating Cl^- in neutral solutions in presence of ethanol.[23]

Mercuric nitrate has been substituted for silver nitrate by many workers, particularly when using sodium nitroprusside as indicator in neutral or acid solutions.[24] Bromophenol blue has been proposed as adsorption indicator for use with mercuric nitrate;[25] also bromocresol green and chlorophenol red may be used.[26] Chloride has been determined in presence of SO_3, S_2O_3, S_2O_6 and NO_2 ions using mercuric nitrate and sodium nitroprusside,[27] the thio-bodies being oxidized by prior treatment with sulphuric acid and potassium permanganate. This technique gives insoluble mercuric nitroprusside at the end-point, and its utility has been confirmed.[28]

With 0·2% alcoholic diphenylcarbazone as indicator,[29] the end-point of the silver nitrate titration is shown by a violet coloration in presence of Cl^-. Diphenylcarbazide has been used as indicator in titrating Cl^- with mercuric nitrate at pH 1·5 – 2·0.[30] In the titration of chloride with mercuric nitrate, diphenylcarbazone as indicator has been found to give a more accurate end-point than does sodium nitroprusside.[31] Solutions as dilute as 0·0005 N-mercuric nitrate have been used with diphenylcarbazide and diphenylcarbazone as indicators.[32] Tetraiodophenolsulphophthalein, used in titrating Cl^- with mercurous nitrate,[33] gives an end-point sharper than that given by bromophenol blue. Mercuric perchlorate has been proposed[34] as a reagent for titrating Cl^- conductometrically, and it may be used also for direct titration with bromophenol blue as adsorption indicator.[35]

A number of methods have been proposed for estimating chloride in special cases. Chlorine, liberated by the action of ferric sulphate, may be absorbed in potassium iodide solution and titrated with sodium thiosulphate.[36] If chloride ion is precipitated with a measured volume of silver nitrate solution, excess Ag^+ may then be removed with a measured volume of potassium iodate solution and after filtering and adding potassium iodide to the acidified solution, the liberated iodine is titrated with sodium thiosulphate.[37] In this reaction one mol. $Na_2S_2O_3 \equiv 6Cl^-$, and the method is accurate to ± 1µg. Another similar technique involves precipitation of excess Ag^+ in the filtrate with potassium iodide,[38] the end-point being shown by the blue colour given by starch in presence of ceric sulphate. In presence of CNS^-, Cl^- may be determined in the filtrate after precipitating the former with copper salts and pyridine to form $[Cu(C_5H_5N)_2](SCN)_2$.[39] From a survey of all the methods used for the determination of chloride,[40] it was concluded that the Gay Lussac gravimetric technique was the most precise, followed by Mohr's volumetric precipitation method in the absence of interfering substances such as ammonium salts.

VOLUMETRIC ESTIMATION OF CHLORIDES ELECTROMETRICALLY

A study has been made of the conductometric determination of free hydrochloric acid in presence of weak acids, e.g. lactic acid, and of mixed halides.[41,42] Much research has been recorded on potentiometric methods for estimating chloride ion particularly by titration with silver nitrate. Titration curves for hydrochloric acid show that accurate results can be attained in presence of colloids,[43] provided these do not remove Ag^+ from solution.[44] The use of a bimetallic electrode consisting of mercury-silver and pure silver has been described.[45] A stabilized anode proposed for this titration consists of a small silver spiral in a solution of nitrates containing gelatin, the cathode being a rotating silver plate.[46] A reference electrode consisting of a buffer solution of chloride, pH 3·00 – 3·03, to which quinhydrone was added has been used;[47] it is connected by a bridge of saturated potassium chloride and 3% agar with a silver electrode, coated with silver chloride by electrolysis, immersed in the sample and used as an indicator electrode. Electrodes of platinum and gold have been used,[48] but the mechanism is not quite clear. A study of the effect of acid concentration indicates that the presence of acid may cause the p.d. at the end-point to differ from the true value by 0·1 V.[49]

By measuring the p.d. between two silver – silver chloride electrodes, one dipping into a solution containing the unknown quantity of Cl^- and the other into a solution containing a known amount, it was possible to determine accurately as little as 0·35 mg. Cl^- per litre.[50] The potentiometric method is well suited to the determination of chloride in the dark coloured waste liquids of the pulp and paper industry.[51] The use of an electronic voltmeter eliminates errors of polarisation.[52] The potentiometric determination of Cl^- in presence of Br^- and I^- may be effected by the controlled use of ammonia at different concentrations.[53] In connection with a determination of the atomic weight of sodium, precise details are given of the electrometric observation of the end-point in the titration of sodium chloride with silver nitrate.[54] A dead-stop end-point electrometric method, using simply two platinum wire electrodes without a reference cell, can be applied to silver titrations of chloride if sodium nitrite is added as anodic depolarizer.[55]

Mercurous nitrate has been employed to titrate Cl^- and Br^- using a mercury electrode.[56,57] Mercurous nitrate always contains some mercuric nitrate which is reduced on the electrode to mercury. The use of mercurous perchlorate, which is easily obtained free from mercuric salts, is recommended. The electrode consists of amalgamated platinum gauze. Cl^- can be titrated with mercuric perchlorate as well as with mercurous perchlorate.[58]

Electrolysis has been used indirectly to determine the halogens[59] by depositing chlorine on a silver electrode at less than 0·59 V. under controlled conditions; this was then made the cathode in dilute caustic soda solution until hydrogen was liberated freely and after washing and sintering at 500°C. the loss in weight of this cathode represented halogen. Precipitated silver halide may be dissolved in potassium cyanide solution which is then electrolyzed; the cathode is weighed to obtain indirectly the halogen present in solution.[60,61]

The method of coulometric analysis has been applied to determine hydrochloric acid in solution, using a platinum cathode and silver anode.[62] After adding potassium chloride, the solution was electrolyzed until the pH lay between 3·8 – 5·4 and the quantity of electricity used was measured on a silver coulometer. The error was less than 0·02%, as against 0·04% by titration with potassium bicarbonate. A similar technique for the determination of halides[63] employs a silver anode and a carefully controlled potential,[63] the current being stopped when the halogen has reacted quantitatively with the silver Several workers[64] describe an amperometric titration of mixtures of halides with a rotating platinum electrode. The method is less accurate than the potentiometric method but much speedier.

A study of the anodic polarization of the halides has been made by connecting the dropping electrode with the positive terminal and the large electrode with the negative terminal of the electrolyser containing 0·1 N-potassium nitrate[65] and it was found[66] that Cl^- showed an anodic step at the potential of the calomel electrode. In many cases Cl^- could be determined at concentrations below 0·004 N., and 5 μg. Cl^- per ml. could be determined with an accuracy of ± 2%. A polarographic titration of an alcoholic chloride solution may be made with lead nitrate solution added from a microburette [67]

THE MICRO DETERMINATION OF CHLORINE

Some simplification of Pregl's original method of elementary analysis has been described,[68] and a micro Carius tube, heated in a bath of methyldiphenylamine rather than in a bomb furnace, has been used.[69] A study of the micro Carius method for halogens shows that the difficulty or ease of the analysis depends upon the structure of the compound analysed.[70] Other workers have continued to suggest improvements on the original method of Pregl;[71, 72, 73] some advocate the sodium peroxide – sugar fusion method in a micro bomb, while others [74] prefer the Carius tube method and give precise details for its use, showing [75] that 5 – 6 drops of nitric acid in the tube followed by heating for 30 min. eliminates any troubles due to explosions.

The Pregl method was modified [76] by sealing a quartz absorption tube vertically to the end of the combustion tube, so that the absorbing solution may be removed without cooling and afterwards drying the combustion tube; while others[77] used the Pregl spiral combustion tube in two sections separated by a ground glass joint used without lubricants. Detailed instructions have been given for using the microtrain in the combustion of highly volatile liquids such as methylene chloride.[78]

A number of variants of the classical Pregl technique have been proposed. Some workers [79] burn a few cg. of material in a stream of oxygen with platinum as catalyst. The halide is titrated with 0·05 N-silver nitrate added from a weight burette using fluorescein and starch as indicator. Excellent results were recorded. Stepanov's method employing sodium and ethyl alcohol was modified[80] by heating the substance under reflux with sodium and ethanolamine, with some dioxan if aromatic compounds were being examined.

Volatile compounds can only be destroyed successfully by mixing them with oxygen and passing them over heated platinum foil and then over a mixture of lime and sodium carbonate. [81] Similar techniques have been used without a catalyst but with a faster flow rate for oxygen (50 ml./min.),[82] in which case halogens are absorbed outside the tube.

The substance may be heated with potassium in a sealed tube when the potassium chloride produced may be determined within ± 0·3%. [83] Aliphatic halides and some aromatic halides when heated with bases such as piperidine or pyridine in sealed tubes at 200°C. for 2 – 3 hours are converted to -onium salts containing ionic halogen which can be determined within + 0·04%.[84] A detailed examination of the Grote-Krekeler micro combustion apparatus has given rise to a number of suggested improvements.[85] The micro (1 – 120 μg. Cl) and ultra-micro (0·25 – 1·0 μg. Cl) determinations of chlorine in organic matter have been further developed.[86]

By treating[87] organic matter with 2 ml. of concentrated sulphuric acid and 0·3 g. potassium dichromate for 20 min. at 150°C., chlorine was expelled and absorbed in 1·5 ml. of 15% caustic soda solution and 0·5 ml. of concentrated sodium bisulphite solution. Excellent results were obtained. Chlorine thus evolved has also been made to combine with hydrogen formed catalytically from hydrazine and palladium in presence of a little caustic potash.[88] Other work on this technique has been reviewed:[89] it confirms that the nickel chromite catalyst used for hydrogenation must be treated with hydrochloric acid to free it from chromic oxide.[89] By working at 400 – 450°C. and titrating the hydrochloric acid produced with standard alkali, a 2 – 5 mg. sample was analysed in a few minutes; the test was sensitive to 1 μg. chloride (or other halogen). For micro quantities of blood or urine, chlorine was liberated by potassium permanganate at 20 – 30°C. and absorbed in 1 ml. 20% potassium iodide solution:[90] the liberated iodine was then titrated against sodium thiosulphate in a Conway burette. Quantities of the order 0·7 to 35 μg. Cl were thus determined.

Because of the difficulties associated with titration of halides on a micro scale, some workers[91] prefer to weigh the chloride as silver chloride after combustion in a micro-bomb. The transfer of the precipitate of silver chloride to the micro-filter is not difficult[92] but is facilitated by the use of a small beaker having a spout containing a fritted glass filter.[93] The possible errors in potentiometric micro titrations of Cl^- with silver nitrate have been pointed out, and methods of making accurate titrations in a final volume of 10 ml. with 0·001 N-silver nitrate have been described.[94] Solutions in alcohol or acetone have been used to avoid the error caused by the solubility of silver chloride in water.[95] Solutions down to 0·0001 N. are titrated in quantities down to 0·25 ml. Other workers[96] similarly considered the solubility of silver chloride to be a decisive factor in the conductometric determination of traces of Cl^-: they determined 0·01 mg. of Cl^- in water and 0·001 mg. in alcohol, at which level the error of the determination was 10%.

A gasometric micro method for the determination of Cl^- in biological fluids has been devised;[97] by its use about 15 determinations per hour can be made with a precision of ± 0·5% in 0·1 ml. of liquid. The solution is shaken with silver iodate and the IO_3^- which replaces Cl^- in solution is estimated by adding alkaline hydrazine and measuring the nitrogen evolved manometrically in a Van Slyke-Neill apparatus (1 $Cl^- \equiv 6$ of oxidized N_2H_4). The IO_3^- could be measured also by adding potassium iodide after acidification (1 $Cl^- \equiv 6$ I): if the iodine liberated was determined colorimetrically 0·0003 mg. Cl^- could be measured.

A colorimetric determination of Cl^- at concentrations of a few mg. per litre has been proposed.[98] Excess of 0·01 N-silver nitrate is added to the solution containing Cl^-, ferric alum and nitric acid, the precipitated silver chloride is removed and an aliquot portion of the filtrate is treated with 0·01 N-potassium thiocyanate; after removing silver thiocyanate, the solution contains red ferric thiocyanate equivalent to the original Cl^- content. The suppression of the colour reaction between mercuric ion and diphenylcarbazide has also been used as a measure of Cl^-;[99] at pH 4, 0·025 mg./l. of Cl^- could be detected and traces of iron and ammonia did not interfere.

By a mercurimetric micro-titration,[100] 0·5 mg./l. of Cl^- was measured with an accuracy of 5%. Mercurous iodate has been proposed for use in the titration (pH 2·2): $Hg_2(IO_3)_2 + 2Cl \rightleftharpoons Hg_2Cl_2 + 2IO_3^-$.[101]

Further work has been done on the nephelometric determination of Cl^- by means of suspensions of silver chloride in 50% ethanol at 40°C.[102] Under these conditions concentrations between 4 and 300 × 10^{-6} M. were determined with an average deviation of 3 to 4%. The effect of various salts on the sensitivity of the method has been examined[103] and the details necessary for the highest precision in a nephelometric method have been described.[104] 0·008 – 0·42 mg. Cl/10 ml. of solution may be measured by adding the sample to a mixture of ethanol, silver nitrate and nitric acid and reading off the turbidity in a Klett nephelometer.[105] A comparison was made with Lamb's method.[102] Furman and Low[106] concluded that electrometric titrations were more accurate, easier to perform and less time-consuming than nephelometric methods and they described a new photronic nephelometer. A Hellige turbidimeter has been employed to avoid the necessity of making reference standards.[107] Using the technique described by Lamb, Furman and others, good results have been obtained on samples containing 0·25 – 5 p.p.m. of Cl^-. Permanent standards made in methyl methacrylate resin are available for measuring Cl^- nephelometrically.

The Tyndall effect and fluorescent photometry have also been proposed for determining traces of halogens.[108]

DETECTION AND DETERMINATION OF CHLORIDE IN PRESENCE OF OTHER HALIDES

A suggestion of Vortmann for the detection of Cl^- in presence of Br^- and I^- has been re-examined.[109] A mixture of silver chloride, bromide and iodide is treated with sodium arsenite solution. The latter reacts solely with silver chloride to give sodium chloride and silver arsenite which is soluble in excess sodium arsenite solution. Upon adding acid to the solution a positive reaction for chloride can be obtained with silver nitrate. Cl^- may be detected in presence of other halides by washing the silver halide precipitate free from silver salt and suspending it in water containing some potassium ferricyanide and a little ammonia.[110] If the silver precipitate contains silver chloride, enough is dissolved to produce a brown precipitate of silver ferricyanide which is much less soluble in ammonia than is silver chloride. A coloration is developed when Cl^-, Br^- and I^- are heated with brucine and potassium persulphate in dilute phosphoric acid.[111] When strychnine is the alkaloid chosen, only Br^- and I^- give colorations; with cinchonidine, I^- alone produces colour.

Traces of Cl^- (or Br^-) in iodides may be determined by adding sodium nitrite and sulphuric acid to the halide solution. After filtering off free iodine and boiling off any dissolved iodine and excess nitrogen peroxide, Cl^- (or Br^-) is determined with silver nitrate.[112] Cl^-, Br^- and I^- may be determined together when each does not exceed 0·3 g. by a procedure[113] which involves *(a)* the determination of I^- by means of potassium iodate, *(b)* the determination of Br^- by means of the reaction $Br^- + HCN + 2\oplus = BrCN + H^+$, and *(c)* the determination of Cl^- by difference or argentometrically after removal of Br^- and I^-.

Oxidation with bromic acid in the presence of hydrocyanic acid, whereby the cyanogen halides are formed, has been employed as a method for the determination of mixed halides.[114]

$$\begin{aligned}
&HBrO_3 + 3\,HI + 3\,HCN \rightarrow 3\,ICN + HBr + 3\,H_2O\\
&HBrO_3 + 2\,HBr + 3\,HCN \rightarrow 3\,BrCN + 3\,H_2O\\
&HBrO_3 + 2\,HCl + 3\,HCN \rightarrow 2\,ClCN + BrCN + 3\,H_2O
\end{aligned}$$

Cyanogen bromide is not formed until all the I^- has been converted into cyanogen iodide. Similarly cyanogen chloride is not produced as long as Br^- or I^- is present. Excess bromate may be destroyed by aniline, phenol or sulphanilic acid, and any cyanogen chloride determined after the following reaction has taken place :-

$$ClCN + 2\,I^- \rightarrow I_2 + Cl^- + CN.$$

After the addition of potassium bromate, I^- and Br^- react also with acetone to form C_3H_5OI and C_3H_5OBr, but Cl^- does not react.[113] To determine chloride, therefore, add 20 – 30 ml. of acetone to 60 ml. of neutral solution and enough sulphuric acid to make the solution finally 1 – 1·5 N. in acidity, and then a slight excess of 0·84% potassium bromate solution (about 3 – 5 ml. excess). Add at once 50 ml. of 5% ferrous sulphate solution and titrate the Cl^- with silver nitrate in the usual way, after adding sufficient 2 N-nitric acid and ferric alum.

Precipitated silver halides may be separated by their decreasing solubility in increasing concentrations of ammonia, in the order silver chloride > bromide > Iodide.[116] Halogens in admixture may be determined on a micro-scale.[117] The silver salts are weighed and then converted either into bromide, or into iodide by heating with the appropriate ammonium salt. I^- is then determined separately by titration with potassium iodate solution. If just sufficient silver nitrate solution is added to precipitate all the I^- and Br^- from an ammoniacal solution and sodium carbonate and arsenite solutions are added to the filtrate which is boiled for 20 – 25 min., the precipitate of silver arsenite may be dissolved in hot concentrated nitric acid and titrated by the Volhard method, thus giving a measure of Cl^-.[118]

Traces of Cl^- may be determined in 1 g. samples of bromide by oxidizing the latter with potassium permanganate at controlled acidity and removing the bromine evolved with acetone. Excess permanganate is removed by hydrogen peroxide and the Cl^- determined with silver nitrate.[119] Similarly freshly precipitated manganese dioxide may be used to release bromine from acid solutions of Br^-.[120] Chlorine is not liberated and after boiling off all the bromine, the Cl^- is determined by any suitable procedure.

The original Berg method (oxidation of hydrobromic acid with bromic acid in presence of acetone to remove bromine) has been modified,[121,122] and if aluminium nitrate is added instead of acetone, bromine must be boiled off before precipitating the Cl^-. Berg's method has been criticized as inaccurate when determining traces of Cl^- in potassium iodide.[123] A preferred technique is to liberate all the iodine by oxidation with potassium permanganate and to remove the last traces of iodine with benzene. The accuracy of the Berg method may be increased by raising the pH of the solution; the normality of the acid for solution should never fall below 1 N.[124]

The electrometric titration of the halides in the presence of one another has been described and a number of empirical corrections have been found necessary.[125] Both silver bromide and chloride are precipitated near the end-point of an electrometric titration so that it is preferable to destroy I^- or Br^- before proceeding with the titration of Cl^-.[126] The halogen hydracids may be measured indirectly by dissolving the mixed silver salts in either concentrated potassium bromide or concentrated potassium iodide solutions. Thus silver chloride and bromide are weighed together and the Cl^- is subsequently replaced by Br^-.[127] The solution is diluted and made acid with nitric acid after which all the silver is precipitated as silver bromide. The Cl^- can then be calculated. Similarly by means of potassium iodide solution all the halides may be converted into silver iodide. Thiocyanates, which are one of the chief interfering bodies in tests for Cl^-, may be removed[128] by adding pyridine and an excess of neutral copper sulphate solution. CNS^- is precipitated as $Cu(C_5H_5N)_2(CNS)_2$. It may be found sufficient to destroy CNS^- or CN^- by boiling with hydrogen peroxide in strong caustic potash solution[129] and this technique is recommended by other workers[130] who find also that boiling concentrated nitric acid will destroy silver thiocyanate but not silver chloride. The bulk of the CNS^- can also be removed by precipitation with lead nitrate and the remainder by boiling with nitric acid and potassium nitrite.[131] The equally troublesome CNSe ion can be removed by precipitation with pyridine and nickel sulphate as $[Ni(C_5H_5N)_4](CNSe)_2$.[132] Traces of this blue compound still remaining in solution may be extracted with chloroform or carbon disulphide. Interference by CN^- may be circumvented by adding 5ml. of 20% formaldehyde to 50 ml. of the mixed salt solution. This solution is then shaken and 5 ml. of 30% nitric acid are added: residual Cl^- may then be titrated by Volhard's method since any cyanide has thus been converted into glycollate and hexamethylenetetramine.[133] If 8 drops of a reagent ($AgNO_3$ 4·25, HgO 2·7 g., HNO_3, *d* 1·4, 10 ml., H_2O 50 ml.) are added to 2 ml. of solution to be tested, an intense turbidity persists even after adding 2 further drops of reagent if more than 1% of Cl^- is present.[134]

THE DETERMINATION OF HYPOCHLORITE AND THE ANALYSIS OF BLEACH LIQUORS

The common bleaching agents (other than chlorites) are so important industrially that their analysis may be considered as a special case, although the analytical techniques employed must be viewed in conjunction with the analysis of hypochlorites in general. A manometric apparatus for measuring the pressure of oxygen evolved when hypochlorites are treated with hydrogen peroxide may be used as a means of estimation.[135, 136] Such techniques are simple and may serve as rapid plant control methods. It has been shown that Penot's arsenite method for the determination of available chlorine in bleaching powder is more accurate than Wagner's iodometric method (potassium iodide and acid) owing to the interference of ClO_3^- in the latter case.[137] If 2 – 4 ml. of 50% acetic acid are added to 25 ml. of solution, the iodometric method then agrees with the arsenite method within 0·2 – 0·3%. A study of the arsenite titration indicates that the end-point is uncertain when potassium iodide starch paper is used as external indicator.[138] It is better to titrate the solution almost to finality, then to add potassium iodide and starch and continue the titration until the blue colour disappears. Another useful procedure is to add excess arsenite solution and, after allowing the liquor to stand for a few minutes, to acidify strongly with hydrochloric acid and titrate back with standard potassium bromate solution using the decolorization of methyl orange to show the end-point.[139] The bleach liquor may be run from a burette into an acid arsenite solution containing methyl orange which is destroyed at the end-point.[140] If bleach liquors are titrated electrometrically it is possible to avoid either reduction of chlorate during titration, or indeed its formation from hypochlorous acid during analysis.[141] Two bright platinum wire electrodes are used, one of them placed in the bleach liquor and the other in the reference electrode, an 8 cm. long tube containing potassium sulphate solution and some titrated hypochlorous acid solution. The electrodes are connected through a high resistance millivoltmeter. Excellent results have been obtained electrometrically using the Penot method of titrating with arsenite solution containing excess of sodium bicarbonate or by the Pontius method of titration in alkaline solution with potassium iodide solution. The use of arsenite solution has been criticized because of its instability and because the presence of ammonium salts causes errors in the titration.[142] For this reason sodium nitrite in bicarbonate solution has been used as titrant, after being standardized against potassium permanganate. Chlorate is not reduced by sodium nitrite.

An apparatus designed for plant control tests on bleach liquor comprises a graduated tube with a lower reaction bulb and an upper stoppered bulb holding 75 ml. of liquid. The reaction bulb is filled with 75 ml. of standard solution of indigo-carmine, the stopper placed in the upper bulb, the apparatus inverted and the burette read. After reversal to the normal position the solution to be analysed is added slowly until the colour of the indigo-carmine changes from blue to light yellow-green. The stopper is then replaced, the apparatus inverted and the burette again read to observe the amount of bleach liquor added.[143] An extensive comparative study of the various volumetric methods proposed for the assay of bleach liquors has shown that differences between all the methods examined are very slight.[144]

The problem of determining free chlorine and hypochlorous acid together in brine has been examined. When the solution is aerated to remove free chlorine the rate of removal is a linear function of concentration so long as any free gas remains. When all free chlorine has gone, further chlorine is formed from the hypochlorous acid and the rate of removal varies as the square of the concentration of the latter.[145] The rate of evolution may therefore be used to measure the original concentration of chlorine.

The Pontius method for determining ClO^-,

$$3OCl^- + 6HCO_3^- + I^- \rightarrow IO_3^- + 3CO_3^{--} + 3Cl^- + 3H_2O + 3CO_2,$$
$$IO_3^- + 5I^- + 3CO_2 \rightarrow 3CO_3^{--} + 3I_2,$$

has been studied by several workers.[146, 147] They conclude that the oxidation to IO_3^- occurs by way of IO^- and that if the titration is rapid this conversion may

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be incomplete so that too much reagent is used.

Schleicher[148] refuted the claim of Clarens that some chlorine dioxide was formed when sodium hypochlorite was titrated with arsenite solution. By means of alkaline arsenite solution hypochlorous acid may be estimated directly and chlorous acid indirectly by reducing a further portion of the solution with arsenite in hydrochloric acid solution.[149] The constituents of a mixture of ClO^-, BrO^-, Cl^-, Br^-, ClO_3^-, BrO_3^- in solution may be analysed by means of arsenite titrations coupled with selective attack on phenol by BrO^-.[150] A proposed indicator for the arsenite titration of hypochlorite is Quinoline Yellow added shortly before the end-point.[151] The change is from yellow–green to colourless. This indicator has also been recommended for use with a specially prepared arsenite solution containing sodium bromide and excess acetic acid.[152]

It has been shown that a modification of the procedure of Treadwell's[141] method for the electrometric titration of hypochlorite can be made satisfactory by the use of a neutral salt alone in the reference electrode cell.[153] Hypochlorite may be titrated potentiometrically in the cold, after adding sodium carbonate with cuprous chloride solution.[154] Chlorate is similarly titrated in strongly acid solution at 80°C. Use of the chlorine electrode in the analysis of hypochlorites has been considered,[155] but it was not found possible to determine the active chlorine in hypochlorite solutions by its use. Methods for distinguishing between OCl^- and N-chloroamines in solution have been studied.[156] Hypochlorite ion is irreversibly reducible at the dropping mercury electrode at all pH values between 3·6 and 11·0 whereas **chloramine-*T*** is reduced more and more slowly as the pH rises. It is thus possible to determine ClO^- in presence of chloramine-*T* at pH 11·0 by the great difference in their rates of reduction by arsenite. A differential method of analysis for mixtures of **chloramine-*T*** and sodium hypochlorite based upon the slow reaction of the former with hydrogen peroxide in alkaline solution, has been devised, which with some modifications may be used when chlorite is present.[157]

Antimony trichloride solution may be used as a reducing agent in hypochlorite analysis:[158] excess antimony is measured by titration with standard potassium bromate using methyl orange as an oxidation indicator. Hot oxalic acid solution has also been used[159] to reduce the ClO^-, as has nitrite solution added to hypochlorite buffered with acetic acid–sodium acetate.[160]

A study of the analysis of solutions containing hypochlorous or chlorous acid[161] shows that it is necessary to determine *(a)* total available chlorine including ClO_2^-, OCl^- and chlorine dioxide by means of potassium iodide and sodium thiosulphate, (*b*) hypochlorite by means of arsenite–iodine, (*c*) total oxidizing power including ClO_3^- with sodium thiosulphate, *(d)* Cl^- with silver nitrate, (*e*) chlorine dioxide by means of sodium thiosulphate, (*f*) acidity or alkalinity.[161] Hypochlorite is reduced to chloride in solutions containing bicarbonate by means of hydrazine sulphate.[162] Potassium bromide is added to the mixed hydrazine sulphate–bicarbonate solution which is then titrated with the hypochlorite solution until free bromine is liberated. This titration gives OCl^-. ClO_2^- and OCl^- are then determined together in another portion with acid potassium iodide and standard sodium thiosulphate.

Hypochlorous acid is sufficiently volatile in a current of hydrogen to decolorize a dilute solution of indigo and may thus be detected: ClO_3^-, ClO_4^- and NO_3^- do not interfere.[163] The acid may be detected in quantities of 0·7 μg. by the colour given by ClO^- with *pp*′-dihydroxytriphenylmethane in neutral or weakly alkaline solutions; many normal oxidizing agents do not interfere.[164]

A distinction between free chlorine and hypochlorous acid lies in the fact that free chlorine oxidises phenolphthalin to phenolphthalein and ferrocyanides to ferricyanides whereas OCl^- does not.[165] Potassium ferrocyanide is added to a solution containing hypochlorous acid and chlorine and is followed by an alkaline solution of phenolphthalin. The liquid turns pink. It is possible thereby to distinguish between waters purified by free chlorine and those treated with chloramines. Chlorine, ozone and OCl^- gave different series of colours with 4:4′-tetramethyldiaminodiphenylmethane;[166] some differentiation of ozone and chlorine etc. is possible by this means. The methods used to distinguish between hypochlorous acid, its salts and free chlorine have been critically reviewed.[167]

It is possible to distinguish between chlorine and chlorine monoxide by absorbing them in potassium iodide solution.[168] Chlorine liberates iodine with no change in acidity, but chlorine monoxide liberates both iodine and hydrogen ions. In order to analyse the mixture, absorb the gas in potassium iodide solution, add a measured volume of sulphuric acid and titrate with sodium thiosulphate, then add excess of potassium iodate and again titrate with thiosulphate.

THE DETERMINATION OF CHLORATE

The use of amalgams to reduce ClO_3^-, BrO_3^- and IO_3^- to Cl^-, Br^- and I^- respectively has been tried.[169] The measurement of the reaction is effected by reducing Ti^{++++} to Ti^{+++} at 60°C. with the excess amalgam. Acid solutions containing ClO_3^- may be titrated directly with amalgam over a period of 3 – 10 min.,[170] or sulphuric acid solutions of ClO_3^- may also be titrated with 0·05 N-titanous sulphate solution electrometrically.

Ferrous sulphate has been chosen as a reducing agent for the titration of ClO_3^-:[172,173] the chlorate ion is quickly reduced at 20°C. in presence of sulphuric acid, and excess ferrous sulphate may be titrated with potassium permanganate. Phosphoric or sulphuric acid may be used to acidify the solution, and after adding an excess of ferrous sulphate solution the excess is titrated, after standing for 10 min. or more, with 0·1 N-potassium dichromate using diphenylaminesulphonic acid as oxidation indicator.[174] It has been said that in order to reduce ClO_3^- with ferrous sulphate the solution must be boiled for 10 min.,[175] though this practice was considered by earlier workers to be unnecessary. Reduction may also be effected with Fe^{++} in 40% hydrochloric acid in presence of a little molybdate catalyst:[176] excess Fe^{++} is then titrated with standard dichromate as described by Williams.[174]

It has been confirmed that the reaction between hydriodic acid and chloric acid is greatly accelerated by Fe^{++}.[177,178] The reaction is also very rapid if the concentration of hydrochloric acid is at least 7·5 N.[179] The reaction is complete in 1 min. with 1·5 times the theoretical amount of potassium iodide. After adding concentrated hydrochloric acid and potassium iodide, iodine may be boiled off and collected in a receiver containing potassium iodide solution.[180] A few p.p.m. of ClO_3^- in caustic soda may thus be estimated, and the various sources of error have been reviewed.

Chlorate in solution may be estimated by adding potassium bromide, 0·1 N-sodium arsenite solution and hydrochloric acid; after boiling for 10 min. the solution is diluted and titrated hot with 0·1 N-potassium bromate using methyl orange as oxidation indicator.[181] Osmium tetroxide has been used as catalyst in this case for the reduction with arsenite,[182] but some workers prefer to titrate ClO_3^- potentiometrically.[183] Various reducing agents have been proposed for the determination of ClO_3^- by volumetric analysis. Among these are uranous sulphate,[184] hot sulphurous acid[185] and vanadous sulphate in an atmosphere of carbon dioxide which gave consistently higher figures than those obtained by ferrous sulphate reduction.[186] The oxidation of thiourea, $CS(NH_2)_2$, to $[NH_2(NH)CS]_2$ by ClO_3^- is the basis of one method.[187] The chlorate solution is added to 20 ml. 18 N-sulphuric acid, 5 ml. of 1% potassium iodide and a measured volume of 0·1 N-thiourea. The mixture is heated at 70°C. for 10 – 15 min., cooled, diluted and titrated with bromate-bromide solution. Chlorate ion may be determined in presence of NO_3^- either by reduction with sulphur dioxide or by sodium nitrite and acetic acid in hot solution.[188] As little as 0·01 – 0·001% potassium chlorate may be detected in nitrates by the coloration given with silver nitrate, hydrochloric acid and aniline. The coloration, which is fugitive (about 10 min.), changes from violet through blue to green. Under certain conditions this test can be made specific for ClO_3^- in presence of BrO_3^- or IO_3^-.[189]

The course of the reaction between ferric salts and chlorates has been studied with the polarograph.[190] The detection of the halogenates each in the presence of the others has been described. ClO_3^- can be detected by heating the solution with zinc and sulphuric acid, whereby free bromine and iodine are expelled, and then testing for Cl^-.[191] A reaction has been proposed for the detection of ClO_3^- in the presence of ClO_4^- and NO_3^-.[192] One gram of fine powder is treated with 5 ml. of freshly prepared H_2S water. In presence of ClO_3^- a turbidity due to sulphur appears within 15 sec. and in 1 – 3 min. the solution becomes white and opaque. ClO_4^- does not show this reaction and it takes at least 10 min. for the same quantity of NO_3^- to show any effect. 10 µg. Potassium chlorate in 0·1 ml. can be detected. A method of detecting ClO_3, BrO_3^- and IO_3^- in admixture with halides by reduction with zinc dust and sulphuric acid has been described.[193]

Several sensitive tests have been proposed for the detection of ClO_3^-. If 1 ml. of solution is evaporated to dryness with 1 ml. 0·5 N-ammonium thiocyanate and the residue heated to 140 – 150°C., an orange red colour develops with more than 0·25 mg. potassium chlorate. ClO_4^- does not give a similar reaction, but IO_3^-, BrO^-, $S_2O_7^-$ and molybdates do so.[194] Difficulties experienced in applying the well-known aniline reaction to the colorimetric detection of ClO_3^- have been noted.[195] Offord[196] uses a modification of Poch's method[194], but employs filter paper impregnated with ammonium thiocyanate; he lists a number of interfering bodies. Autenrieth's test for ClO_3^- using indigo and sulphuric acid is extremely sensitive.[197] This fact is confirmed and it is shown that a specially prepared indigo-carmine solution enables 1 drop (0·060 ml.) of a 0·001% solution of sodium chlorate to be detected.[198] The method is valuable in the detection of ClO_3^- in seeds and roots. A method has been adopted for the determination of ClO_3^- in milk (0·5 p.p.m. of $NaClO_3$; 1 ml.) and serves indirectly for the detection of OCl^-.[199] Milk treated with 78·4% sulphuric acid shows a strong yellow fluorescence in ultra-violet light in presence of ClO_3^-. A little stannous chloride is added to prevent fluorescence due to normal oxidation.[200] About 10 parts of chlorate per million of milk can thus be detected. A drop or two of pyridine sulphate solution added to a chlorate residue in a porcelain dish produces a permanent red colour.[201] Chlorate may be detected in caustic soda solutions by adding a solution of *o*-tolidine hydrochloride to the solution and neutralizing with hydrochloric acid. The yellow colour produced is then measured. Five parts per 10^6 can be measured accurately to within 4% after allowing for interference caused by iron, manganese and copper.[202] Quantities of sodium chlorate of the order 10 – 100 µg. per ml. can be titrated by means of standard methyl orange solution. The results are accurate to within 1 – 2%.[203]

Chlorate may also be detected by the evolution of chlorine dioxide after treatment with concentrated sulphuric acid. The halogen oxide gives a blue coloration with benzidine acetate.[203a] One microgram may be detected at a concentration of $1:10^4$ and 2500 parts of NO_3^- has no effect. NO_2^- must be removed by acid sodium azide solution and halides by the action of silver nitrate.

THE DETERMINATION OF PERCHLORATE

König[204] modified Rothmund's method (the reduction of ClO_4^- by boiling with acid titanous sulphate) by titrating the excess Ti^{+++} salt with ferric alum using thiocyanate as indicator. The best precipitant for ClO_4^- is a concentrated nitron solution.[205] It has been shown that NO_3^-, ClO_3^- and ClO_4^- all give characteristic precipitates with nitron but that by the action of Devarda's alloy in alkaline solution the two former ions may be reduced without affecting the ClO_4^- [206] Heller[207, 208] investigating Gasparini's method of electrolytic reduction of ClO_4^- in concentrated sulphuric acid, found that the electrolysis was slow and ClO_3^- was also reduced. Perchlorate in solution may be treated with boiling arsenite solution acidified with sulphuric acid; excess of arsenite is then destroyed with permanganate and the Cl^- produced from the ClO_4^- is weighed as silver chloride.[209] Perchlorate may be precipitated as its potassium salt in aqueous alcohol by addition of potassium acetate in alcohol.[210] Some modifications are necessary if Cl^-, ClO_3^- or NO_3^- is present. If the perchlorate is heated with excess chromic oxide and sodium carbonate in an atmosphere of carbon dioxide for 20 min. and finally ignited for 20 min., the CrO_4^- produced may be determined iodometrically after adding potassium iodide to a solution of the melt.[211] Tetraphenylarsonium chloride is suggested as a precipitant for ClO_4^-,[212] though other ions, such as MnO_4^-, IO_4^- etc., are also precipitated. A solution containing ClO_4^- can be titrated potentiometrically against this reagent.

Perchlorate may be determined in the presence of much ClO_3^- and Cl^-.[213] Chlorate, but not perchlorate, is reduced with sulphur dioxide which is readily expelled by boiling; the ClO_4^- ion is then reduced with titanous chloride in an inert atmosphere. If perchlorates are treated with concentrated sulphuric acid and an oxidizing agent such as potassium persulphate, the gases evolved being caught in sodium sulphite or similar solution the resulting Cl^- may be determined potentiometrically with silver nitrate.[214] The gases evolved in the distilling flask are mainly chlorine peroxide. By modifying the procedure, mixtures of ClO_3^-, ClO_4^- and Cl^- can be analysed.

Traces of ClO_4^- in crude nitrate are determined by precipitation as the perchlorates of organic compounds containing quaternary ammoniacal groups such as malachite green, crystal violet or (Hofmann's reagent) methylene blue.[215] Hahn used 20 ml. zinc sulphate solution, *d* 1·35, and 5 ml. of 0·001 M-methylene blue as reagent. Five ml. of this solution was shaken with 0·2 ml. of 20% solution of nitrate and compared with colour standards containing 0 – 1·0% of potassium perchlorate. After 1 hr., differences of 0·01% of perchlorate can be detected.

Fedorova[216] modifies Hahn's reagent to allow for the detection of ClO_4^- in ClO_3^- and shows that 0·001% potassium perchlorate can be detected in a mixture of 1% potassium chlorate and 99% potassium nitrate. She also shows[217] that Hahn's reagent is superior to Hofmann's reagent (*loc. cit.*) because it is simpler to use. The method is employed to detect 3 μg. of ClO_4^- or 0·01% perchloric acid in cellulose acetate.[218] It is pointed out[219] that the use of methylene blue as laid down by Monier does not give accurate results and better directions for its use are given. Methylene blue and picric acid are used for the volumetric microdetermination of ClO_4^- [220]

Behrens' test for the detection of perchlorate is recommended.[221] Rubidium perchlorate is formed on a microscope slide from rubidium chloride solution alkaline with sodium bicarbonate. After careful drying but while barely dry, 1 – 2 drops of potassium permanganate solution are added and the residue is dried again until crusts form. Microscopical examination can then detect 0·1% potassium perchlorate. Traces of perchloric acid (0·0001 – 0·001%) in spent accumulator acid may be determined by reducing with titanous sulphate and titrating the hydrochloric acid formed with mercuric nitrate solution and sodium nitroprusside indicator.[222] Perchlorate present in biological fluids may be estimated with titanous chloride solution, the excess of which is titrated against 0·01 N-ferric chloride solution;[223] the relationship, 8 mol. of titanous chloride per mol. of ClO_4^-, is particularly favourable.[224] It has been shown that the colorimetric method of Krüger and Tschirch[218] is specially suited for determining sodium perchlorate in sodium nitrate and for mixtures of sodium perchlorate and chlorate.[225]

The various methods for the determination of perchlorates have been compared and the defects of each pointed out.[226] The colorimetric method of Hahn (*loc. cit.*) and the method of Spitalsky and Jofa (*loc. cit.*) are recommended for traces.[227] Nichols[228] challenges the statement (Mellor, II, 381) that perchlorates are reduced by titanous chloride while chlorates are not.

THE DETERMINATION OF CHLORITE

Chlorites may be titrated electrometrically by means of sodium thiosulphate after potassium iodide has been added to the sulphuric acid solution[229] and most of the titrimetric methods devised for ClO^- will also serve to determine ClO_2^-.[230] To determine ClO^- and ClO_2^- in admixture in a single sample, ClO^- is measured potentiometrically with sodium arsenite solution alkaline to caustic soda; excess of the alkaline arsenite solution is then added and the sample neutralized to methyl orange. Concentrated hydrochloric acid is then added to obtain a 4% solution and the sample is back titrated with 0·1 N-potassium bromate. This second procedure allows the determination of ClO_2^- to be made:[231] ClO_3^- present in concentrations below 1% does not interfere.

Chlorites may be titrated potentiometrically in a cold solution by means of ferrous sulphate: the solution is made slightly alkaline and sodium acetate is added.[231a] Chlorite can also be determined in presence of ClO_3^- by a titrimetric procedure, but the ClO_2^- is high by 2% when ClO_3^- is 1-N.[232] As little as 0·1 mg. of hypochlorite may be determined in presence of ClO_2^-, ClO_3^- and Cl^- by titration of the ammonia evolved when the mixture is steam-distilled with an alkaline solution of aminoacetic acid.[233] Even with a large excess of ClO_2^- the error does not exceed 1 – 6%. The paper gives a useful general discussion of methods for the analysis of commercial chlorites.

Chlorites may be detected by adding a neutral carbon dioxide-free solution to mercuric nitrate whereby a red precipitate of mercuric chlorite is formed; other chloro acids do not react similarly.[234] A few ml. of a 0·1% solution of *p*-phenetidine acidified with formic acid is covered with ether and shaken with 1 – 3 drops of the chlorite solution: if chlorite is present a clear violet colour develops in the aqueous solution, any coloured compound produced by ClO^- passing into the ether.[235]

The analogous constitution of chlorites and nitrites may be used as a means of identifying the former.[235a] Thus the coloured products obtained with the three primary, homologous diamines may be coupled with an amine or a phenol, and in this way 5 μg. of ClO_2^- may be detected in a drop of solution. The method succeeds in presence of ClO_3^- but not in presence of ClO^-. A green colour given by chlorite in an acetic acid solution containing copper is unaffected by the presence of ClO_3^- or ClO^-: 25 μg. of ClO_2^- can thus be detected in a drop of solution.

Dissolved chlorine dioxide in solutions of Cl^- and ClO_2^-, may be determined by utilizing the fact that ClO_2^- is not reduced at a mercury cathode;[236] chlorine dioxide is reduced so rapidly that the mercury drop is coated instantly with Hg^I compounds and then functions as a Hg/Hg^{++} electrode. A mixture of chlorine, monochloroamine, chlorine dioxide and ClO_2^- in water can be analysed by four amperometric titrations with standard arsenite at pH 7. One sample is titrated after hydrolysis at pH 11; another, also hydrolyzed at pH 11, is treated with potassium iodide just before titration; the third is titrated in presence of potassium iodide without previous hydrolysis and the last is treated with potassium iodide at pH 2 and then buffered at pH 7 for titration.[237]

THE DETERMINATION OF HYPOCHLORITE, CHLORATE AND PERCHLORATE IN ADMIXTURE

If ClO^- is first titrated with arsenite solution in the cold in 5% hydrochloric acid, ClO_3^- may then be determined by a further similar titration after raising the acidity to 10 – 12% and boiling; perchlorates do not interfere.[238] Similarly it is possible to determine ClO^- and ClO_3^- together in boiling solution and ClO_3^- alone after decomposing hypochlorite with ammonium chloride.[239] When ClO^- is determined with arsenite, another portion of the sample may be reduced with the same amount of arsenite after buffering with boric acid and sodium borate to pH 7·4, the total chloride is titrated potentiometrically with silver nitrate: the original Cl^- is then calculated by difference.[240]

Chloride ion may be titrated in dilute acid solution with mercuric nitrate solution and sodium nitroprusside as indicator: ClO^- is then reduced with an acid arsenite solution and the above procedure is again carried out: finally ClO_3^- is reduced to Cl^- by boiling with sodium nitrite solution and the Cl^- is again determined.[241] If ClO_3^- is reduced with acid formaldehyde, ClO_4^- may be determined in the filtrate after precipitating all the Cl^- as silver chloride.[243] Chlorate and perchlorate in brines are determined by reducing ClO_3^- with Mohr's salt and titrating excess Fe^{++} with ceric sulphate. The solution is rendered ammoniacal to remove iron and cerium and after acidification excess titanous sulphate is added to reduce ClO_4^- to Cl^- and the excess is titrated with ceric sulphate.[243] Alternatively, Cl^-, ClO_3^- and ClO_4^- may be measured in admixture by precipitating Cl^- with silver nitrate, reducing ClO_3^- with zinc, and finally heating the dry residue with manganese nitrate and potassium carbonate to reduce ClO_4^- to Cl^-.[244] A mixture of ClO_3^-, BrO_3^- and IO_3^- may be analysed as follows:-[245] the ions are reduced with zinc in boiling neutral solution: any iodine is liberated from the mixed halides by ferric ammonium alum solution and is distilled into cold potassium iodide solution; bromine is liberated by means of lead peroxide in dilute acetic acid solution and is distilled into potassium iodide solution. These reactions leave Cl^- unattacked.

THE DETERMINATION OF CHLORINE IN ORGANIC MATTER

A number of simple combustion methods for the determination of chlorine in organic matter have been proposed. Thus the vaporized sample may be mixed with air and passed through a quartz tube heated to at least 900°C. The chlorine is absorbed in caustic soda solution, any chlorate is reduced and the halogen is determined by the Volhard method. The method is rapid and very accurate.[246] The advantages of the classical Grote-Krekeler method in modernized form have been pointed out.[247, 249] A rapid determination of chlorine in coal is made by heating 0·5 g. of the latter in a fast stream of oxygen at 1350°C. Chlorine is absorbed on a silver spiral immersed in water;[248] or, preferably, the chlorine may be absorbed in ammoniacal hydrogen peroxide and titrated potentiometrically.[249]

Several workers favour the use of a catalyst in the quartz combustion tube and the Swedish method of Klason, in which a platinum gauze catalyst is used and the substance is heated in a stream of nitric acid vapour, has advantages.[250] The versatility of the Dennstedt method of combustion using oxygen and a platinum gauze catalyst has also been demonstrated.[251] Air containing a little ammonia has been used to burn organic matter, the mixture being passed over heated copper oxide.[252] Platinized asbestos is sometimes preferred to gauze, and Dennstedt's design of combustion apparatus is also advocated as it tends to prevent explosions.[253] A platinum spiral has also been used in the Dennstedt procedure,[254] the substance being weighed in an ampoule with a capillary opening. Of the other dynamic methods of combustion proposed, heating the substance in a platinum boat in a quartz tube in a stream of hydrogen and ammonia has been suggested.[255] After removing hydrogen cyanide in the absorber by boiling with acetic acid, Cl^- is titrated by the Volhard method. Explosive substances are mixed, prior to combustion, with six times their weight of oxalic acid. The method has been commended, though cyclic halogen derivatives are not always decomposed and it is probably better to use air in place of hydrogen. A catalytic hydrogenation method with copper or silver catalysts has also been proposed.[256]

Among the static methods used for destroying organic matter, the use of chromic acid is popular. For example, the substance in the reaction vessel is covered with a large amount of potassium dichromate and cooled sulphuric acid is run in very rapidly, the mixture being cooled in ice if necessary.[257] Hydrocarbons and fully chlorinated bodies are completely oxidized by chromic-sulphuric acid mixture.[258] This is true of saturated acyclic carbon compounds and the evolved chlorine may be absorbed in alkaline hydrazine:[259] in cases where the technique is applicable, the greatest deviation of a result from average is 1%. Persulphates may be used as the active oxidizing agent[260] and concentrated nitric acid is frequently employed.[261, 262] It is necessary to keep the material in contact with nitric acid for some hours prior to heating, but some materials still present certain difficulties. Saturated permanganate solution and concentrated nitric acid may similarly be used.[263]

The reaction between organic chlorine and sodamide has been used by a number of workers for the estimation of the halogen.[264] The material is dissolved in liquid ammonia, with the aid of ether if necessary, and sodium is added; when the reaction is complete, 5 g. of ammonium nitrate in a little liquid ammonia are added; the chlorine is determined in the residue by the usual methods.[265] A blue colour must persist in the liquor for at least 30 min. after adding the sodium.[266,267]

The ashing of organic matter generally results in the loss of some chlorine as confirmed by a series of papers on the subject. The loss through this cause may be 30% of the total chlorine[268] but the use of lime greatly reduces the loss. There is a loss of sodium chloride or potassium chloride on incineration.[269] Ashing in presence of sodium carbonate is advantageous provided the sodium carbonate : chloride ratio is greater than 5,[270] but some loss can occur even in presence of carbonate.[271] The temperature of ashing in the presence of sodium carbonate should not exceed 600°C.[272]

Some workers[273] prefer to treat the substance in a nickel crucible with five times its weight of fused caustic potash, while others heat in a closed tube with solid permanganate.[274] By the latter method the results are precise and the chlorine contents of hexachlorobenzene and phenyl derivatives are more readily determined than by the Carius method.[284] About 0·2 g. of sample may be treated with 7 g. of sodium peroxide in a nickel crucible cooled in water; the lid of the crucible is weighted with 150 g. of lead and the reaction is initiated with a hot nail.[275] Alternatively, about 0·15 g. of sample is heated with 0·5 g. of potassium or sodium in an evacuated tube for 15 – 30 min. at 400°C.[276] Hot oleum can serve as liquid reagent for the destruction of organic matter.[277]

The calorimetric bomb recommended by Berthelot has been employed,[278] using a substance of high calorific value (0·5 ml. decalin) and placing 5 – 10 ml. concentrated ammonia in the bomb. It is preferable to wait 30 min. after firing before opening the bomb. The normal bomb calorimeter used for coal combustion will also serve.[279] The sodium peroxide-sugar explosion method is reliable and accurate and it can be applied to volatile liquids such as chloroform.[280] Kimball and Tufts[281] modify the method of Elving and Ligett by heating the substance with potassium in a nickel bomb at 500 – 550°C. for 2 hr.

Alternatively the substance may be burnt on the cotton wick of a lamp and the products of combustion absorbed in an alkaline absorbent.[291] A variety of more elaborate lamps with silica wicks are also in common use.

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The original Stepanov method for halogens (using sodium and alcohol) has been modified by using 3 – 4 ml. of decalin and sodium:[282] after standing for 12 hr. the sample is refluxed for 2 hr., cooled and the excess sodium is destroyed with alcohol. A critical study of the method has elucidated the numerous conditions that must be satisfied in order to get good results,[283] and the technique has been applied to micro-quantitative determinations (3 – 10 mg.).[284]

Gasparini's electrolytic decomposition technique for organic substances is found to be of limited use:[285] the substance is treated with concentrated nitric acid and electrolyzed at 125 v. and 0·5 – 1 amp. for 1 – 4 hr. with platinum electrodes.[286] It is said that by using monoethanolamine as a reagent for removing halogen, alkyl halogen can be determined in presence of aryl halogen.[287] If 0·1 – 0·2 g. of substance is treated with 30 – 50 ml. of alcohol, 10 ml. of 10% caustic potash in alcohol and 3 g. of 1% palladiumised calcium carbonate followed by 10 drops of hydrazine sulphate and the mixture is boiled under reflux for 30 min., Cl^- can be determined after filtering off the catalyst.[288] Compounds may be reduced with hydrogen in presence of acetic acid, sodium acetate and copper sulphate as catalysts, hydrogen being generated by reaction between zinc dust and the acetic acid.[289] Dehalogenation may also be effected by means of zinc (2 g.) in alkaline solution (20% caustic soda 10 ml., 10 ml. methanol) in the presence of Raney nickel (0·5 g.).[290]

THE DETERMINATION OF CHLORINE IN WATER

Much work has been done on the determination of free chlorine in water and on the differentiation of chlorine from mono- and di-chloroamines and from nitrogen trichloride. The starch–iodide test for chlorine, normally sensitive to 0·2 p.p.m. may be used to detect 0·1 p.p.m.[292] Some prefer the use of Raschig's benzidine solution for the determination of chlorine. A 0·1% solution of *o*-tolidine in fairly strong hydrochloric acid is much used for the colorimetric estimation of small quantities of chlorine in chlorinated water supplies. Under standard conditions this reagent gives a yellow coloration the depth of which depends on the proportion of chlorine present[293] and may be matched against permanent standards that are, conveniently, dilute aqueous solutions of dichromate modified in colour by small additions of copper sulphate.[294]

The starch–iodide and *o*-tolidine tests are thought to be about equally sensitive, but the latter is preferred because fewer substances interfere with it.[295] The effect of changes in pH on the tolidine coloration (excess acid is necessary for its stability) have been studied[296] and an improved reagent has been described[297] which is favourably received by other workers.[299] Manganese behaves like free chlorine in the test[298] and others have drawn attention to this scource of error,[300] manganic and not manganous ion producing the colour.[301] If chlorine is boiled off from a second sample of water the difference in colour obtained on the original and on the boiled water should show the true chlorine content. The serious interference due to nitrites in this test has also been noted.[302]

The interference by manganese has been discussed[303] and it is suggested that it may be avoided by precipitating the manganese with caustic soda using magnesium hydroxide (from added sulphate) as a carrier.[304] Even 0·01 p.p.m. of nitrite will react with *o*-tolidine[305] and to avoid this it is proposed that thiosulphate be added beforehand or that the nitrite be oxidised by hydrogen peroxide.[306]

There are many weaknesses in the *o*-tolidine test and it probably needs further study.[307] As little as 0·1 p.p.m. Fe^{+++} may cause an erroneous figure for chlorine,[308] though some workers state that Fe^{+++} when present at less than 0·3 p.p.m. does not interfere.[309] The ferric ion may be complexed

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by adding basic sodium pyrophosphate.[310] It is possible to use the retarding effect of sodium arsenite on the colour reaction and thus to eliminate interference by Mn^{+++}, NO_2^- and Fe^{+++}.[311] This test will also differentiate between free chlorine and chloroamines. It is said that if 0·5% sodium arsenite solution is added 15 sec. after the *o*-tolidine, it neutralizes all combined chlorine before it can react with the tolidine (Step *A*). By adding sodium arsenite before *o*-tolidine (Step *B*), all chlorine, free and combined, is eliminated, but interfering bodies still give colour. Free chlorine is then assessed by (Step *A* – Step *B*).[312] The arsenite solution used should be acid to methyl orange.[313]

Both the *o*-tolidine reagent and the copper sulphate-potassium dichromate standards must be protected from light[314] and auric chloride has been proposed as a permanent colour standard.[315] At pH below 2, the yellow colour of the reagent has a characteristic minimum at 436 mμ.[316]

The *o*-tolidine test is used to assess the chlorine demand in the break-point chlorination of water[317] and one can titrate the water with standard *o*-tolidine solution at pH 1·8, until no further yellow colour appears;[318] this method is as accurate as the *o*-tolidine-arsenite colorimetric method. Another method[319] is to add 100 ml. of sample to sodium hexametaphosphate and neutral *o*-tolidine in a titration flask and titrate with standard Fe^{++} solution until the blue colour is discharged (this gives $Cl_2 + \frac{2}{3}NCl_3$): then potassium iodide is added and the titration continued to obtain monochloroamine and followed with dilute sulphuric acid and sodium bicarbonate to obtain dichloroamine. Nitrogen trichloride is determined in a second sample by extraction with chloroform, determining chlorine in the aqueous layer, subtracting this from the reading of free chlorine and multiplying the result by 1·5. In one investigation[320] it was found that of 50 compounds examined, *o*-tolidine proved the most satisfactory for the detection of chlorine.

It has been suggested that 0·1% dimethyl-p-phenylenediamine in acetic acid solution may be used for the determination of chlorine down to 0·03 mg./l.[321] All weak oxidizing agents give a red colour with the reagent which works best at pH 2·6 – 3·4:[322] the presence of phosphoric acid is said to avoid certain difficulties,[323] but some workers consider that this modification gives no better results than the use of 30% tolidine.[324]

The use of a 5% solution of p-aminodimethylaniline for the detection of bromine, iodine or chlorine is proposed[325] and is thought to merit further study.[326] When the reagent is buffered to pH 6·8, chlorine gives a red coloration, but chloroamine does not. If potassium iodide is then added, chloroamine also reacts. For quantities of 0·5 p.p.m. or less, the results are within 0·02 p.p.m. of the truth.[327, 328]

It is shown that free chlorine, but not chloroamine or alkaline hypochlorite, will bleach methyl orange;[329] and a similar bleaching effect on methyl red (0·1 g./l.) has been used for the determination of 0·04 – 8 mg./l. chlorine.[330] The reaction is, however, a slow one. A sensitivity of 0·1 p.p.m. chlorine in solutions of pH less than 3 has been claimed using methyl orange, and it was shown that Mn^{+++}, but not chloroamine, interfered.[331] This technique has been adapted to a micro-scale.[332] Other workers, using methyl orange solution containing hydrobromic acid, were able to determine chlorine in the range 0·02 – 0·5 mg./l.[333]

Among less known indicators, the use of α-naphthoflavone has been proposed.[334] If acid fuchsin, a trace of potassium bromide and acetic acid are added to the sample, the pink colour produced will enable 0·005 – 0·7 mg./l. chlorine to be measured.[335] The purple tint produced by *p*-aminodimethylaniline and free chlorine has been used[336] but Fe^{+++} and NO_2^- both interfere with the method. Any diamino compound of the type 3:3′-dimethyl-4:4′-diaminodiphenyl dihydrochloride used at pH 4 is a suitable reagent.[337] Tris(*p*-dimethylaminophenyl)methane trihydrochloride, which gives a violet colour (crystal violet) with free chlorine, shows some specificity; 0·1 mg./l. of chlorine can readily be detected, but the colour is only given by chloroamines after boiling for 5 min. with the reagent.[338]

Because of the shortcomings of the popular *o*-tolidine test for chlorine, potentiometric methods of measurement have been proposed.[339] Similarly water has been titrated amperometrically with sodium arsenite using sodium chloride as the electrolyte.[340] Chlorine present as chloroamines is found by adding potassium iodide to the sample, re-determining the end-point and subtracting free chlorine from the total residual chlorine; Fe^{+++}, Mn^{+++}, and NO_2^- do not interfere. A useful and specific test for chlorine (or bromine) has been described:[341] 1% sodium cyanide added to the water produces cyanogen chloride and if 25% pyridine containing 2% benzidine hydrochloride is then added an intensely coloured di-anil derivative is formed.

THE DETERMINATION OF FREE CHLORINE AND CHLORO BODIES IN THE ATMOSPHERE

Chlorine may be detected in the air by its action on potassium iodide deposited on silver leaf 3μ thick:[342] enough iodine is produced to form silver iodide and to break an electrical circuit. A conductometric cell may be used to measure the electrical resistivity of water taken from an air scrubber: the resistivity falls as chlorine is absorbed.[343] If a measured volume of air is passed through 10 ml. of 0·1% *o*-tolidine in dilute hydrochloric acid, the yellow colour produced may be matched against standards of copper sulphate and potassium dichromate solutions.[344] Resorufin reacts with chlorine or bromine to form a blue, non-fluorescent solution and the loss in fluorescence may be used to measure these halogens.[345] The colourless body, 2:5-bis-(2:4-dimethyl-N-pyrryl)-3:6-dibromohydroquinone, is oxidized to a blue quinone in alcoholic solution by oxidizing agents such as bromine or chlorine, and 0·002 mg. of bromine or chlorine may be detected in this way.[346,347]

The detection and determination of organic halogen derivatives present in the atmosphere have been investigated by several workers using Beilstein's flame test. If air is passed at 1·5 l./min. through a heated quartz tube containing a roll of oxidized copper gauze and the gauze is subsequently inserted in a colourless flame, the strength and duration of the green flame coloration indicates the quantity of halogen absorbed.[348] Using a micro-atomizer and a hydrogen flame on a copper wire, 5 μg. of chlorine as chloroform can be detected.[349]

An alcohol lamp fitted with copper gauze may be used[350] or a Bunsen burner, also with 10 sq. cm. of gauze, whereby 30 p.p.m. of chlorine as vinyl chloride may be detected.[351] Some recommend a tube of Monel metal.[352,353] A halide detector lamp burning pure ethanol and a blow lamp using methanol as fuel have also been proposed.[354]

Hydrogen chloride, phosgene or carbon oxybromide may be detected in the atmosphere by the orange yellow stain they give on cotton impregnated with a mixture of p-dimethylaminobenzaldehyde and diphenylamine.[355]

MISCELLANEOUS PHYSICAL METHODS FOR THE DETERMINATION OF CHLORINE

By using the relevant absorption coefficient of a beam of monochromatic *X*-rays it is possible to determine chlorine in solution in the presence of other halogens with a relative error of less than 1%.[356] The *X*-ray absorption of gaseous chlorine has been measured and it is shown that the results may be of analytical interest.[357]

Much work has been done on the direct spectrographic detection and determination of chlorine. If material is sparked directly in the usual high voltage spark with the electrodes surrounded by pure carbon dioxide to eliminate air lines, it is possible to detect 0·5% chlorine and 0·3% bromine.[358] By employing ultra-high frequency excitation in the region 4100 – 7100 A, 0·1% chlorine in potassium bromide and 0·03% bromine in sodium chloride are detected with an accuracy of ± 5 – 10%.[359] The use of a hollow cathode source applied to the spectrographic analysis of the halogens permits the detection of 0·01 μg. of fluorine and 0·2 μg. of chlorine.[360] The spectrographic determination of halides is reviewed[361] and an a.c. arc with a large capacity shunt in a circuit with low self-inductance is recommended. Both electrodes are of copper and the solution is allowed to drip on the lower one. The lines 4904, 4819, 4810, 4794 are recommended for chlorine.[361]

An easy and rapid method has been described.[362] 10 – 20 mg. of sample are placed in a high-melting glass tube evacuated to less than 0·001 mm. mercury. The spectrum is excited without electrodes in the high frequency field of a coil of 10 turns surrounding the tube. All the halogens can be detected together down to at least 0·01% and sometimes to 0·001% with an accuracy of 10%. In another procedure the solution to be tested may be allowed to drip into an a.c. arc through an opening in a copper tip used as a lower electrode. The various sensitivities of suitable lines for chlorine and bromine have been listed.[363] Alternatively, the powder sample may be deposited on a massive copper bar moistened with collodion and amyl acetate. The bar is then dried at 120°C, and installed as the lower electrode, while a cone-shaped copper upper electrode is fitted about it. As the arc (a.c.) burns, the lower bar is automatically moved in a horizontal plane below the upper electrode. A circuit diagram and list of suitable lines are described.[364] The conditions of the circuit are defined very precisely in order to obtain a suitable spark discharge, but the technique described is not considered to be sufficiently accurate for quantitative work.[365]

Quantities of the order of 5 μg. of chloride on fabric may be measured spectrographically using the intensity of the aluminium chloride band at 2610 A.[366]

Among other physical methods of determining chlorine, some workers measure the extinction coefficients of Cl^- at λ 436, 454 and 463 $\mu\mu$ and Br^- at $\lambda = 463$ $\mu\mu$ in aqueous solution.[367] Mixtures of chlorine and bromine in water may thereby be analysed. If a sample is subjected to neutron bombardment, any Cl^-, Br^-, or I^- will be transformed respectively into radioactive chlorine with half-life of 35 min., bromine with a long period and iodine with a period of 25 min.[368] By adding a little inactive halide and precipitating with silver nitrate, the three original halogen concentrations are estimated. The chloride group anions, including CNS^-, may be separated by partition chromatography on paper,[369] using butanol saturated with 1·5N-ammonia as the solvent. After the bands have been developed by means of silver nitrate, 0·1 mg. of halogen can be identified.

MISCELLANEOUS ASPECTS OF CHLORINE ANALYSIS

The normal exposure of a silver chloride precipitate to light causes no appreciable loss of weight,[370] but positive or negative errors occur if silver or halide respectively are present in excess when the precipitation itself is not protected from light. Under an arc light, during 5 hr. stirring, the error was 0·6% of the weight, but in general it was 1 in 500.

Chlorine in sulphur chlorides may be determined indirectly by its reaction with β-naphthyl ethyl ether; sulphur monochloride and dichloride do not react with this reagent.[371]

Mixtures of chlorine phosgene and nitrosyl chloride may be analysed by means of their action on mercury.[372] Chlorine is completely absorbed, nitrosyl chloride yields 1 mol. of nitric oxide and phosgene does not react. Free chlorine in phosgene may be determined by means of mercuric iodide, with which it reacts to liberate iodine at room temperature, while there is no reaction with phosgene: 0·01% chlorine can thus be determined.[373]

Specifications and methods of analysis for liquid chlorine have been discussed[374] and the conclusion is reached that organic impurities should not exceed 0·01%.

Hydrochloric acid is in common use as a primary or secondary standard in chemical analysis. Temperature correction tables have been published for this acid.[375] Methods for preparing exactly 0·1N-hydrochloric acid are described[376] and in this connection the use of a mixture of 1 of sodium carbonate to 10 or 20 of anhydrous sodium sulphate has been proposed, as keeping better and being weighed more easily than sodium carbonate alone.[377] Other workers prefer to standardize the acid by precipitating it as silver chloride.[378] Other proposals are to dissolve 0·2 – 0·5 g. of crystalline sodium thiosulphate in water, to add 2 ml. of a 4% potassium iodate solution, 0·3 g. of solid potassium iodide, 1 ml. starch solution, to dilute to 100 ml. and to titrate with the hydrochloric acid solution until the colourless solution becomes blue.[379] The rapid and accurate preparation of the decinormal acid has been further studied.[380]

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SECTION XX

BIOLOGICAL PROPERTIES OF CHLORINE

By G. M. DYSON

The irritant and toxic nature of chlorine and its extensive industrial use have led to a number of serious or fatal cases of poisoning. There is some disparity between the values given by various authors for the permissible and toxic concentrations of chlorine in inspired air. Elkins[1] gives the limit of 1 p.p.m., and Drinker[2] gives 0·1 - 2 p.p.m. for the upper limit of chlorine permissible in air for continual breathing without adverse effects. Rumpel[3] gives a lower figure, stating that breathing an atmosphere containing 0·05 mg./l. of chlorine leads to serious effects in ½ - 1 hour. This is confirmed by Freitag[9] who gives the figures:-

Concentration (mg./l.)	Effect
0·01	Can be breathed for several hours without effect.
0·1 - 0·15	Lethal in 1 - 1½ hours.

Shire[4] gives a concentration of 3 mg./l. of chlorine as rapidly fatal to small animals.

Chlorine reacts on the upper respiratory tract and the lungs;[5] œdema of the lungs with abnormal release of sugar[6] is observed during chlorine poisoning, and the general alteration of the composition of the body fluids during chlorine intoxication has been studied.[7] It is found that chronic intoxication with chlorine may accelerate tubercular processes in animals.[8] Administration of oxygen and minimization of bodily effort are the essential first-aid measures in chlorine poisoning, followed by immediate medical attention. Poisoning by chlorine has been described in many instances;[10-13] in one case a railway tank containing 15 tons of liquid chlorine exploded[14] and eighty-five persons were severely poisoned, of whom three died. There is no known instance of criminal poisoning with chlorine; all records refer to accidental poisoning, which has led to many publications[15-25] dealing with the hazards of large-scale operations with chlorine and the measures to be taken to minimize these risks. It is not possible completely to survey this aspect of the subject; many of the precautions are best described as 'engineering good-housekeeping', such as using for liquid chlorine containers which will withstand the pressure likely to be generated by direct sunshine in summer; using completely gas-tight pipework and vessels; providing very good ventilation and protective water sprays, etc. One potent source of danger in chlorine systems is the very high coefficient of cubic expansion of liquid chlorine. Thus, a section of pipe between two closed valves will, if completely filled with chlorine, burst on rise of temperature solely owing to this factor.[30] One useful adjunct[31] to the use of chlorine in the laboratory is the use of rigid polyvinyl chloride tubing; plasticized tube has a much shorter life. This tubing has an almost indefinite life in chlorine at ordinary temperatures. It may be softened sufficiently, by warm air or with 1,2-dichloroethyl acetate, to make bends or to make connexions to glass tubulures. The softening fluid soon evaporates. A stopcock lubricant which will resist chlorine is made[31] by heating glycerol with half its weight of sucrose at 120° until the latter is dissolved, and grinding the clear mixture with 10% of its weight of graphite.

The poisonous action of chlorine on micro-organisms affords an important means of disinfection. In water treatment the use of small quantities of chlorine with or without ammonia has become standard practice, and by using higher halogen concentrations the bacterial count of effluents from industrial plants can be controlled, as for example, in citrus fruit canneries,[32] in the control of bacteriophage in dairy cheese-starters[33] and in general dairy practice. Where, as in kraft-paper production,[34] organisms resistant to chlorine are encountered, chlorine dioxide has often proved effective.[35]

Many authors have described in detail the activity of chlorine towards various micro-organisms; it is now fairly conclusively proved[36] that the mode of action is by complete inhibition of the sulphydryl enzymes of bacteria, leading to their death. The sensitivity of aldolase from *Escherichia coli* to chlorine is of the correct order of magnitude to correlate with the bactericidal activity of the halogen.

Much disinfection is carried out with hypochlorite solutions, which offer a convenient mode of application of the halogen. They are not quite so effective as the free halogen[37] and their activity diminishes with excess alkalinity;[38] thus, a given neutral solution of sodium hypochlorite at pH 7·2 kills 99·9% of organisms in 4 seconds, but requires 8 seconds under similar conditions at pH 10·5. The presence of ammonia[39] often enhances the activity of chlorine and hypochlorites; this is presumed[39] to be due to the action of chloroamine[40] (NH_2Cl).

The continued use of hypochlorite solutions in bleaching and disinfection can give rise to dermatitis,[13] which is largely due to the alkali present; to avoid this, and at the same time to achieve higher stability, it has been proposed to use N-chloro or N-dichloro derivatives of organic compounds. For example, chloramine-T[42,43] has been used in dairy sterilization, especially in the routine cleaning of milk bottles; and recently[41] 1,3-dichloro-5,5-dimethylhydantoin has been used very successfully in all branches of dairy sterilization. The latter compound is freely soluble in water, contains 16% of available chlorine and is comparable in bactericidal activity with hypochlorite, with the added advantage that it is effective at pH 5·8 – 7·0. It has far less odour than hypochlorite solutions.

The activity of chlorine in the destruction of organisms more complex than bacteria has been investigated from two main viewpoints. The first is the destruction of non-pathogens such as *Crenothrix* in pipe-lines[44] where their growth can reduce considerably the hydraulic capacity; for this purpose 1–3 p.p.m. of chlorine in the water is sufficient. In the second application, successful attempts have been made to kill the cysts of *Entamoeba histolytica*[45] and the active cerceriæ of *Schistosoma mansoni*[46] by chlorination at 0·2 – 1 p.p.m. An additional use is the treatment of seeds for destruction of the spores of smut or bunt and for protection from weevils. Dry seeds appear[47,48] to need a 2 hour exposure to a 3 – 10% concentration of chlorine for effective disinfection.

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CHAPTER III

BROMINE

SECTION XXI

THE OCCURRENCE AND EXTRACTION OF BROMINE.

By A. G. SHARPE

Several investigations of the bromine content of plant and animal products have been reported in the past thirty years. The bromine content of cow's milk is 18·4 – 24·1 γ per 100 c.c.,[1] of human blood, 358 – 583 γ per 100 c.c.[2] Sponges may contain up to 2·5% of bromine,[3-5] human hair about 0·5%,[6] and vegetables rather widely varying quantities (0·05 – 2 mg.%).[7,8] Russian workers have given data for the concentration of bromine in soils ($0{\cdot}1 - 4{\cdot}0 \times 10^{-3}$% of the dry weight),[9] and river waters ($6{\cdot}8 \times 10^{-7} - 8{\cdot}15 \times 10^{-6}$%).[10] The Cl : Br : I ratio was found to be 8600 : 27 : 1 in river waters and 7900 : 27 : 0·021 in sea water.[10] Plants grown on poor soil in dry climates were found to contain about ten times as much bromine as those grown on rich soils in temperate climates.[10] Wheats contain 0·001 – 0·0075 g. of bromine per kg. and flours 0·003 – 0·0055 g. per kg.[31]

The occurrence of bromine in the Stassfurt carnallite deposits has led to determinations of the bromine content of carnallites from Utah, in which up to 0·3% was found,[11] from New Mexico (0·1%),[11] and Solikamsk, Russia (0·15 – 0·3%);[12, 13, 103-105] the average bromine content of German carnallites is 0·2 – 0·35%. The bromine content of a number of primary rock-salt deposits has been found to vary between 0·005% and 0·04%;[14] the geochemical significance of distribution of some sixteen elements, including bromine, has been discussed by Correns.[15]

Analyses of many brines, mineral waters, and sea waters have been summarised by Blake;[32] some of these were reported previously (Mellor, II, 16). More recent determinations include those on the oil-bearing waters of the Caucasus and the marine muds of the Black, Kara, and Barents Seas (0·0025 – 0·007% Br).[16] The bromine content of mineral, coal, and bituminous deposits increases with increase in the amount of organic matter present;[17] and it seems likely that the element is brought in by the accumulation of halide in the leaves of trees during a forest succession.[18] Underground brine from Falsa Pan (South Africa) contains up to 0·016% Br;[19] the 'Los Gauchos' spring (Buenos Aires) has a bromine content of 0·378 g. per litre.[20] In the Gulf of Riga and the Baltic Sea the bromine content varies with depth, place, and season between 8·55 and 21·8 p.p.m.; the Br : Cl ratio, however, remains constant at 0·0034 : 1.[21] A similar ratio (0·00347 : 1) has been reported for the North East Pacific Ocean.[22]

The bromine contents of the Cheshire salt deposits and of inshore waters round Great Britain have been extensively investigated. The soluble matter (75·3% of the dry weight after drying at 100°) of the Cheshire deposits has a mean bromine content of 0·0223% Br; the Br : Cl ratio varies considerably with depth.[107] In representative brines made by artificial solution of the deposit the bromine content varies from 97·6 to 150 g. per cubic metre, the Br : Cl ratio from 1 : 1310 to 1 : 1939.[107] Data for total salinity and bromine content of sea waters have been obtained for several sites at different states of the tide;

the usual value is about 65 g. Br per cubic metre. The highest salinity was recorded off Cornwall; at Hale, in Cornwall, and Amlwch in Anglesey, plants for the extraction of bromine have been erected.[108]

In South Australia, lake water contains 5 – 270 p.p.m. of bromine, sea water 70 – 131 p.p.m., and brines 350 – 5600 p.p.m.[23] In the Sea of Japan the bromine content is 59 – 66 p.p.m. and is unaffected by depth or distance from the shore.[24] Irkutsk salt brines contain 69 – 91 g. of bromine per cubic metre;[27] oil-well waters of the Grozny district, up to 143 mg. per litre.[29] In the Gulf of Karabugaz and nearby salt lakes, the water contains 0·01 – 0·07% bromine, the value being lowest in spring and highest in autumn; the bromine reserves of this source are about 25 × 10^6 tons.[96] Searles Lake brine contains about 0·085% of bromine, but the alkalinity is too high for its economic extraction from this source.[102]

Data on the bromine contents of other brines,[30,116] mineral springs,[87,88] oil-well waters,[90,98,106] salt lake waters,[28,84,85,91-95,97,99-101] and salt beds [25,26,89] have also been published. The influence of source of supply on the Cl : Br ratio in underground waters has been discussed; waters with Cl : Br about 300 : 1 are considered to be derived from normal sea water; those with higher Cl : Br ratios may be formed by leaching of chloride-rich salt deposits.[86]

All methods of any importance for the manufacture of bromine continue to be based on displacement from bromide-containing solution by chlorine. The extraction from the mother liquor remaining after the separation of potassium chloride from carnallite (the Kubierschky process) has already been described (Mellor, II, 39); more descriptions of this process have been given, but only minor modifications have been introduced.[33,35,38,39,46,50,72,109] The working of carnallite-crude salt deposits containing tachhydrite and kieserite has now been made possible: treatment with a cold waste liquor containing magnesium chloride dissolves most of the tachhydrite and some of the kieserite, and simultaneously extracts most of the bromide, which may be recovered by treatment with chlorine in the usual way.[37] Although the continuous process for the preparation of elementary bromine (Mellor, II, 39) has displaced the iron bromide process, much Fe_3Br_8 is still manufactured by interaction of scrap iron, steam and bromine vapour; this salt still affords the most convenient means of preparing soluble bromides.[34,111] By far the most important use of free bromine is in the manufacture of ethylene dibromide; much smaller quantities are used in analysis, in synthetic organic chemistry, for the purification of swimming-pool water, and in the shrink-proofing of wool.[54,117-119]

In the extraction of bromine from fairly rich sources, the heating of large volumes of solution to 70 – 80° is not prohibitive in cost; but in the extraction from a very dilute solution such as sea water, a process which became important after 1918, heating must be avoided. One early method involved the chlorination of sea water and the interaction of the liberated bromine with aniline sulphate; the sparingly soluble tribromoaniline was separated in filter presses.[40-42,47,110] Decomposition of the tribromoaniline has not been described.

The interaction of bromine and phenol, whereby tribromophenol is precipitated, has been used in a Russian process. When bromine reacts with phenol according to the equation

$$3Br_2 + C_6H_5OH = C_6H_2Br_3OH + 3HBr$$

half of the bromine is lost as hydrogen bromide; by carrying out the bromination with a regulated addition of chlorine, however, 98% of the bromine may be separated as tribromophenol.[43,45] It was at first claimed[43] that treatment of of the tribromophenol with dilute nitric acid gave recovery of 98% of the bromine (the other product being picric acid), but later workers failed to substantiate this claim,[44] and the tribromophenol had to be decomposed by fusion with caustic soda.[45]

By far the most important process used for obtaining bromine from sea water, however, is that operated by the Dow Chemical Company, first at Wilmington, North Carolina, and later at Freeport, Texas. Sea water is pumped to the top of a brick tower; on the ascent it is treated with sufficient sulphuric acid to bring the pH down to 3·5 and with a 15% excess of chlorine. As the liquid descends, a current of air is blown through it, and the mixture of air and bromine vapour is then allowed to react with sulphur dioxide and steam. The spray of mixed sulphuric and hydrobromic acids is collected; the bromine is again liberated by the action of chlorine and is collected as in the steaming-out process. The dilute sulphuric and hydrochloric acids formed are used for acidifying the sea water in the first stage of the process. The whole process is automatically controlled, the rate of addition of chlorine being governed by measurement of the oxidation potential of the liquid with a platinum electrode. A high initial temperature of the sea water clearly favours extraction of the bromine by diminishing its solubility in water, and this consideration explains the location of both plants. This process has been the subject of a number of patents (*e.g.*,[48-53]); a general authoritative account of it, with references, has been given by Stenger.[54]

Before the introduction of sulphurous acid for the recovery of bromine from the air stream, absorption of the halogen was usually carried out using sodium carbonate solution. The resulting solution of sodium bromide and bromate was acidified with sulphuric acid, and bromine was steamed out.[54-56] Variations of this procedure have been reported from other countries, and it is generally claimed that the yield of bromine is 90% or greater.[57-61] Solvent extraction has also been suggested for collection of the bromine, and the use of carbon tetrachloride,[62,63] tetrachloroethane,[62] carbon disulphide,[62] and ethylene dibromide[62] has been advocated. The bromine may be separated from the organic solvent by fractional distillation[62] or by treatment with slaked lime;[63] the latter yielsd a product analogous to bleaching powder which is decomposed by acid with liberation of all of the bromine.[63] It has been stated that addition of up to 30% of benzene to carbon tetrachloride gives improved results in the extraction.[114] Amongst other methods mentioned in the literature for recovery of bromine in this and other processes are the following: absorption from the air stream (previously dried by calcium chloride) by silica gel;[64] absorption by ferrous bromide, followed by decomposition of the resulting ferric bromide by chlorine;[65] absorption by unsaturated hydrocarbons,[66,67] including 'crude gasoline';[67] interaction with silver, followed by solution of the silver bromide in potassium bromide solution and electrolysis;[68] absorption by activated charcoal, followed by liberation of the bromine by treatment with steam.[69-71]

Two other processes for the preparation of bromine from brines are described in the patent literature. In one of these, designed for alkaline brines, carbon dioxide is dissolved in the brine under pressure, reducing its pH to below 4·4; an oxidising agent is added, and reduction of the pressure then effects liberation of the bromine along with the carbon dioxide. After absorption of bromine from the gas, the carbon dioxide is recompressed and used again.[73] A preliminary electrolytic oxidation of brine, followed by acidification, has also been suggested as the first part of the separation.[74,75] For more concentrated solutions of bromides, nitric acid may be used as the oxidising agent.[76] Electrolytic recovery using copper or silver anodes and a potential difference of 1·75 – 1·9 V.,[113] and the oxidation of hydrogen bromide by oxygen over metal oxide catalysts at temperatures between 325° and 1000°,[77,78] have also been investigated.

Bromine may be freed from chlorine by distillation from metal bromides (Mellor, II, 40), passage through a layer of a solid bromide,[115] fractional condensation from an air stream carrying the mixed vapours at a temperature considerably below the boiling point of bromine,[114] or passage over charcoal impregnated with ferric oxide or alumina.[79] Iodine-free bromine pure enough

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for microchemical work may be prepared by repeatedly shaking the liquid with a large quantity of water.[80] The preparation of highly pure bromine suitable for atomic weight determinations is discussed later (see page). Bromine may be dried by passage through or contact with concentrated sulphuric acid; for bromine, so dried, satisfactory containers may be constructed of iron, zinc, nickel, or Monel metal.[81-83] Teflon or Fluon (polytetrafluoroethylene) is also inert, and is a suitable material for gaskets exposed to bromine.[82]

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SECTION XXII

THE PHYSICAL AND CHEMICAL PROPERTIES OF BROMINE.

By A. G. SHARPE

STRUCTURE, IONIC AND COVALENT RADII

Solid bromine (which, contrary to earlier reports, is now stated[11] to have an orange colour at −252°) forms a molecular lattice.[1] The unit cell is orthorhombic, with a = 4·48, b = 6·67, and c = 8·72 A., and contains four molecules. The calculated density at −150° is 4 05, in satisfactory agreement with experimental values of 4·107 at −195°[2] and 4·13 at −253°.[3] The space group is *Ccma* (V_h^{18}); the Br–Br distance in the molecule is 2·27 ± 0·10 A., and each bromine atom has next nearest neighbours at 3·30 (two), 3·75, 3·98 (two), 4·00 (four) and 4·10 (two) A.[1] There is no evidence to suggest that allotropes of bromine exist.[10]

The interatomic distance for the Br_2 molecule in solid bromine agrees well with the values of 2·28 A.[4] and 2·279 A.[6] obtained for bromine vapour by the method of electron diffraction. The single covalent radius of bromine is accordingly generally taken to be 1·14 A. The simple additivity principle for covalent radii appears to hold for most bromine-containing compounds for which structural data are available: *e.g.*, C–Br in CBr_4 and CH_3Br is 1·91 A.[5] (mean of C–C in diamond and Br–Br in Br_2 = 1·91 A.); P–Br in PBr_3 is 2·23 A.[7] (mean of C–C and P–P in P_4 = 2·20 A.). The lengths of bonds formed by bromine have therefore attracted relatively little attention; this subject has been discussed by Wells.[14] The tetrahedral radius of the bromine atom is estimated to be 1·11 A.[8] Effective radii of covalently-bonded atoms have been discussed from another point of view by Theilacker, who starts from the assumption that for covalent (as for ionic) compounds the co-ordination number of the middle atom of a group is governed by the radius ratio of the two types of atom. This approach leads to a value of 1·62 A. for the 'effective radius' of bromine;[154] 'effective radii' of this kind do not by summation give observed interatomic distances, and their value appears to be severely limited.

Physical data relevant to the evaluation of the radius of the bromide ion, and the assumptions involved in various attempts at this evaluation, have been reviewed by Pauling, who concludes that the best value is 1·95 A.[9] This value appears to be universally accepted.

VAPOUR DENSITY AND DENSITY

The vapour density between 87·7° and 112·4° has the values shown in Table I.[12] Barometric pressure in these determinations varied from 745 to 752 mm. The values for vapour density are 1–2% higher than those calculated assuming ideal gas behaviour. The compressibility factor to be applied to *PV* values calculated from the perfect gas law has been estimated, using the Hougen and Watson chart and the reduced pressure and temperature, to be 0·992 – 0·993 in the range of temperature and pressure studied.[12]

No recent determination of the specific gravity of bromine at room temperature has been reported, but values at 25·15° (3·1006), 30·15° (3·0836), 34·45° (3·0689), 39·85° (3·0499), 44·35° (3·0345), 47·85° (3·0227), and 51·55°

TABLE I.-VAPOUR DENSITY OF BROMINE

t (°C.)	87·7	89·2	91·4	91·7	98·8	99·6	101·2	110·9	111·4	112·4
d_t (g./l., at atm. pressure)	5·480	5·406	5·322	5·333	5·217	5·196	5·168	5·045	5·084	5·038
PV (l. atm., at 1 atm.)	28·85	29·03	29·48	29·49	30·08	30·27	30·32	31·09	30·94	31·11

(3·0093) have been given.[155] From the specific gravities of solid bromine at 20°K. (4·13)[3] and 79°K. (4·107),[2] the extrapolated value at absolute zero is 4·17.[2] The extrapolated atomic volume at absolute zero is given as 19·3 c.c.[3] and 19·2 c.c.[2,13] An attempt has been made to correlate the molecular volumes of bromine and other substances with the rates of their attack on metals.[156] It has also been suggested that there is a relationship between molecular volume, boiling point and constitution for bromine-containing organic compounds.[21]

CRITICAL CONSTANTS

A direct determination of the critical temperature and a short extrapolation to obtain the critical pressure of bromine gave values of 311° and 102 atm.[15] These differ from the formerly accepted values (Mellor, II, 52); and since a recent evaluation of the critical volume[12] was based on $T_C = 575$°K. and $d_C = 1{\cdot}18$ g./c.c. (giving $V_C = 0{\cdot}1355$ l.) it, too, may require correction. The relationship of critical constants, including those of bromine, to degree of molecular association at the critical point has been briefly discussed by Lautié;[16] attempts have been made to treat critical pressure as an additive property, but without any considerable success.[157,158]

SURFACE TENSION, VISCOSITY AND RELATED CONSTANTS

From the data for surface tension and density (Mellor, II, 50) the parachor for molecular bromine is 132; the parachor for bromine in organic compounds, however, has been variously reported as 68,[18] 68·5,[18,159] 68·8 [19] and 69.[20] The interpretation of parachors, including that of bromine, has been considered, and it has been concluded that Sugden's view that it is a measure of molecular volume is justified;[159] relationship between surface tension and internal pressure have also been discussed.[160,161]

Newer results for the viscosity of liquid bromine agree well with those of Thorpe and Rodger (Mellor, II, 50). In the range -4·3° to +32°,

$$\eta_t = \eta_0/(1 + 1{\cdot}2257 \times 10^{-2}t + 2{\cdot}721 \times 10^{-6}t^2).$$

The viscosity at 0° is 0·01241 c.g.s. units; that at the b.p., obtained by extrapolation, is 0·00717 c.g.s. units.[22] Experimental values have been compared with values calculated on theories of the liquid state.[23-25]

The viscosity of bromine vapour (Mellor, II, 50) has been extensively investigated by Braune, Basch and Wentzel,[26] whose results differ somewhat from those of Rankine (Mellor, II, 50) over a limited range of temperature, and are shown in Table II (see page 697). Above 460°K., their results may be expressed by the equation:-

$$\eta_T = 236{\cdot}6 \times 10^{-7} T^{3/2}(T + 532{\cdot}8)^{-1},$$

showing that in the temperature range 460–867°K., the Sutherland relationship holds.[26,27]

The rheochor[28] for bromine in organic compounds is variously given as 35·8[28] and 13·8.[29] The molecular volume at zero fluidity is said to be an

TABLE II.- VISCOSITY OF BROMINE VAPOUR

$\eta \times 10^4$	t°K.	$\eta \times 10^4$	t°K.	$\eta \times 10^4$	t°K.
1·526	292·0	2·097	411·0	3·476	683·0
1·574	292·2	2·369	463·0	3·525	693·6
1·542	293·5	2·500	484·0	3·591	712·0
1·535	294·0	2·626	515·0	3·967	789·1
1·530	296·5	2·698	524·2	4·106	808·0
1·528	298·0	2·999	589·0	4·300	861·0
1·921	369·0	3·163	622·5	4·292	867·0

additive function, the contribution from a bromine atom in organic compounds being 23·0.[147] Attempts have also been made to find relationships between liquid fluidity, volume, pressure and temperature;[30,31] between viscosity, density and chemical constitution in organic liquids;[32] and between viscosity, molecular weight, specific gravity, and structure.[146]

VAPOUR PRESSURE, BOILING POINT AND MELTING POINT

The vapour pressure of bromine between -9·6° and 303·1° is represented, according to Scheffer and Voogd,[15] by the equation:

$$\log p \text{ (in mm.)} = -2087{\cdot}0\, T^{-1} - 3{\cdot}449 \log T + 17{\cdot}871.$$

Values obtained by this equation, however, are a little too high at low temperatures.[15] These values (up to the b.p.) are somewhat higher than those of Ramsay and Young (Mellor, II, 53) and give the b.p. of bromine at 760 mm. pressure as 58·4°. Two direct determinations of the b.p. of carefully purified bromine gave 58·80 ± 0·1° (on the hydrogen scale of temperature) or 58·88 ± 0·1° (on the mercury-in-glass scale),[33] and 58·8°,[34] the latter value at 760·5 mm. Since Ramsay and Young gave the b.p. as 58·75°, their results over the temperature range -5° to 58° are probably still the best available. For solid bromine the values in Table III have been recorded.

TABLE III.- VAPOUR PRESSURE OF SOLID BROMINE

t (°C)	−95·5	−63·1	−50·3	−46·1
p (mm.)	0·002[37]	0·26[37]	1·12[37]	1·71[37]
t (°C)	−32·0	−21·1	−15·5	−10·9
p (mm.)	6·44[37]	15·76[38]	24·95[38]	35·37[38]

The first five results fit the equation[37]

$$\log p = -12150/T^{1{\cdot}368} + 7{\cdot}5030;$$

the last three fit the equation[38]

$$\log p = -7109/T - 43{\cdot}3 \log T + 133{\cdot}47.$$

A differential method for the measurement of vapour pressure,[35] and the use of the Clusius-Dickel separation tube with helium as inert gas between the bromine and a mercury manometer,[36] have given results concordant with those quoted above.

Reported changes in the physical properties of bromine and other liquids after intensive drying[39-41] must be regarded as unconfirmed.[42-44] As Hinshelwood[45] has pointed out, it is inconceivable that addition or removal of a trace of foreign substances should alter thermodynamic properties in bulk.

The empirical quantity $M \log_{10} T + 8{\cdot}0\, M^{-1}$, where M = mol. wt. and T = b.p. in °K., seems to be an additive function for many organic liquids; the contribution for a bromine atom is 255.[46]

The accepted value for the melting point of bromine remains −7·2 ± 0·1°; this figure has been compared with those calculated on hole theories of liquids.[47,48] The cryoscopic constant per 100 g. of bromine has been found experimentally to be 8·31°; that calculated from the m.p. and latent heat of fusion is 8·64°.[49] The triple point is variously given as −7·3° and 46·4 mm.,[38] −7·3° and 44·1 mm.,[37] and −7·6° and 43·1 mm.[15]

THERMODYNAMIC PROPERTIES

The specific heat of bromine at low temperatures has been measured by Latimer and Hoenschal.[50] Some of their values are given in Table IV.

TABLE IV.- SPECIFIC HEAT OF BROMINE AT LOW TEMPERATURES

T (°K.)	14·9	17·3	23·3	29·9	48·6	65·5
C_p (g.-cal. mole^{-1})	1·83	2·36	3·82	5·18	7·96	9·38
T	88·1	93·5	98·5	116·5	152·7	175·4
C_p	10·06	10·30	10·38	10·94	11·80	12·26
T	183·0	209·3	217·8	244·2	250·6	252·4
C_p	12·54	13·12	13·24	14·02	14·24	14·36

Values have also been recorded by Suhrmann and von Lude;[51] their results are rather higher than those of Latimer and Hoenschal, e.g., at 154·9° K. they give $C_p = 12{\cdot}64$ g.-cal. mole^{-1}.

Regnault's value of 2·53 kg.-cal.mole^{-1} for the latent heat of fusion at the m.p. (Mellor, II, 54) is in satisfactory agreement with values obtained by subtracting the latent heat of vaporization of liquid bromine (see below) from the latent heat of sublimation of solid bromine. The latter, calculated by Wohl from the vapour pressure curve for solid bromine,[37,38] is 10·4 ± 0·2 kg.-cal. mole^{-1} at the m.p.[59] Since Regnault gave the m.p. of bromine as −7·32°, there seems little reason to doubt his result. The value attributed (Mellor, II, 55) to Andrews for the specific heat of bromine at constant pressure between 11° and 45° should read 0·111. No new determination of the specific heats of bromine vapour has been reported. Both specific heats (C_p and C_v) are higher than those for permanent diatomic gases, and the ratio C_p/C_v is therefore low (1·29). This is now generally attributed to vibration within the molecule, which for bromine is important even just above the boiling point; values calculated on kinetic theory for a rigid diatomic molecule are thus too low. Attention has been directed to the fact that for bromine, as for many other substances, C_v (liq.) $\sim C_v$ (gas), indicating that the rotational and vibrational partition functions are approximately the same for the two phases.[62]

Theoretical values for the heat capacity of bromine vapour in the range 300–1500°K. have been calculated[57] and may be expressed approximately (to within 0·2–0·7%) by the equation:[162]

$$C_p = 8{\cdot}4228 + 0{\cdot}974 \times 10^{-3}T - 3{\cdot}555 \times 10^{-7}T^2.$$

From among several concordant results the best value[52] for the latent heat of vaporization at 25° is 7·34 kg.-cal. mole^{-1}. From the vapour pressure curve the value at the b.p. is 7·24 kg.-cal.mole^{-1} (calculated from the results of Ramsay and Young) or 7·27 kg.-cal.mole^{-1}.[15] Taking the latent heat of vaporization at the b.p. as 7·25 kg.-cal.mole^{-1} and the b.p. as 58·8°, the entropy of vaporization is 22·0 g.-cal. deg.$^{-1}$ mole^{-1}; the significance of this value has been discussed in terms of restricted rotation of the molecules in the liquid phase.[63] The heat of condensation at 10°, determined calorimetrically, is 46·7 g.-cal. g.$^{-1}$ or 7·47 kg.-cal. mole^{-1}.[53] From the vapour pressure data given for liquid bromine near 0°, the latent heat of vaporization is calculated to be 7·55 kg.-cal.mole^{-1} [18] or 7·83 kg.-cal.mole^{-1} (based on the result of Ramsay and Young; Mellor, II, 53).

From calorimetric data the standard molal entropy of liquid bromine (at 25°) has been evaluated[50] as 36·8 ± 0·4 g.-cal. deg^{-1}; the earlier value given

(Mellor, II, 56) refers to a g.-atom and should be doubled. From this figure the calorimetrically obtained standard molal entropy is 59·5 g.-cal. deg^{-1}.[163] This quantity may be obtained with very much greater accuracy from spectroscopic data:[54-57] the two most important computations give 58·63[54] and 58·67[57] g.-cal. deg.$^{-1}$ mole^{-1}. The U.S. Bureau of Standards selected value is 58·639 g.-cal. deg.$^{-1}$ mole^{-1}.[52] Thermodynamic data for Br_2(liq.), Br_2(g.), and Br(g.) in the spectroscopic state $^2P_{3/2}$ at 25°, taken from this critical compilation, are:

	ΔH°	ΔG°	S°
Br_2 (liq.)	0	0	36·4
Br_2 (gas)	7·34	0·751	58·639
Br (gas)	26·71	19·69	41·805

(ΔH°, ΔG° in kg.-cal. mole^{-1} or kg.-cal. g.-atom^{-1};
S° in g.-cal. deg.$^{-1}$ mole^{-1} or g.-cal. deg.$^{-1}$ g.-atom^{-1})

The chemical constant for molecular bromine, obtained from spectroscopic data, is +2·35 (this value refers to the calculation of vapour pressures in atmospheres)[58] Experimental values include 2·86,[59] 2·79,[90] 2·59 ± 0·1,[58] 2·55 ± 0·1,[51] and 2·5 ± 0·25.[60] For monatomic bromine the values obtained are 1·87 (spectroscopic),[58] 1·88[61] and 1·89 ± 0·2.[60]

IONIZATION POTENTIAL AND ELECTRON AFFINITY

Earlier estimates of the first ionization potential of bromine were discussed by Noyes,[64] who, from a study of the potential necessary to maintain luminosity in bromine vapour, suggested a value of 12·5 ± 0·5 e.v. A detailed investigation of the arc spectrum of bromine indicated a value of 11·80 e.v.[65] The most recent values are 11·844, 21·584, and 35·890 e.v. for the first, second, and third potentials respectively.[66,67] Extrapolation along the series Cu, Zn, Ga, Ge, As, Se is reported to suggest a value of 109 e.v. for the seventh potential, but there is no experimental confirmation of this.[68] With copper *X*-radiation of mean wave-length 1·38 A. the potential required for formation of an ion-pair is 27·9 e.v.[69]

Many investigators have evaluated the electron affinity of bromine from the Born cycle, using calculated lattice energies for alkali metal bromides and experimental data for the other quantities involved (a general account of the method is given by Moelwyn-Hughes).[89] The precise value obtained for the electron affinity depends largely on the degree of refinement attempted in the evaluation of the lattice energy. Representative values obtained by this method are 84,[77] 87,[78] 77·2[79] and 87 ± 2·5[73] kg.-cal. g. atom^{-1}. The most accurate result afforded by this method is probably that of Mayer and Helmholtz,[80] who found the electron affinity of bromine to be 81·5 kg.-cal. g. atom^{-1}.

Several other methods have been used for the determination of the electron affinity of bromine. Measurement of the conductivity of a flame fed with ethyl bromide indicated a value of 86·7 kg.-cal. g. atom^{-1}.[71] From the appearance potential of the Br^- ion in a mass spectrographic analysis of bromine, Blewett deduced a value of 87·6 ± 4 kg.-cal. g. atom^{-1}.[74] The determination from the space-charge effects of a hot tungsten filament in bromine vapour gave 88 ± 3·4 kg.-cal. g. atom^{-1}.[70] By determining the heat of ionic dissociation of alkali metal bromide vapours from measurement of the degree of ionization at different temperatures, and by combining these heats with other thermochemical data, lattice energies can be obtained experimentally; from the values so obtained, application of the Born cycle method has given results of 84[76] and 80[75] kg.-cal. g. atom^{-1}, based on measurements of the ionization of rubidium,[76] potassium,[75] and sodium[75] bromides. Sutton and Mayer developed a method for the direct evaluation of the electron affinity of iodine, based on measurement of the equilibrium between iodine atoms, iodide ions, and free electrons in the gas phase;[72] and by a refinement of this method Doty and Mayer determined the

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electron affinity of bromine as 80·5 ± 0·4 kg.-cal. g. atom^{-1}.[81] The good agreement between this figure and the result obtained by the most accurate Born cycle method strongly suggests that Doty and Mayer's value is the best at present available. There is no trend in the electron affinity in the pressure range 0·39 – 21·2 μ between 1607° and 2276° K.[81]

THE ELECTRONEGATIVITY OF BROMINE AND THE ENERGIES OF BONDS INVOLVING BROMINE

A discussion of the meaning of the term 'electronegativity' has been given by Pauling,[9] who also discusses the various experimentally measurable quantities in terms of which electronegativities may be evaluated. One of the two principal authors on this subject (Mulliken)[82] defines electronegativity as the mean of first ionization potential and electron affinity. The value for bromine on this scale is 2·75, obtained by dividing the sum of ionization potential and electron affinity by 130 (on this scale, F = 4·06, H = 2·52).[9] Pauling's electronegativity coefficient, x, is calculated from the difference between the observed bond energy in a heteronuclear diatomic molecule AB and the arithmetic mean of the A–A and B–B single bond energies (on this scale, $x_F = 4{\cdot}0$, $x_{Br} = 2{\cdot}8$, $x_H = 2{\cdot}1$).[9] Relationships, usually of a semi-empirical character, between some or all of the quantities bond energy, bond lengths, electronegativity, and force constants have been discussed by several authors.[83-88] Linnett[87] gives 2·5 and 4·1 × 10^5 dynes/cm. for the force constants of the Br–Br bond in Br_2 and the H–Br bond in HBr.

HYDRATION ENERGY AND NUMBER OF THE BROMIDE ION

As Latimer[91] pointed out, the sum of the hydration energies of the cation and anion of most salts must be approximately equal to the lattice energy, since heats of solution of salts are usually small. In principle, the hydration energy of an ion is calculable from its radius in aqueous solution, its charge, and the dielectric constant of the medium.[92] Because of the difficulty of determining the quantities necessary for such a calculation, the first attempt to obtain the hydration energy of the bromide ion made use of the somewhat questionable value for the absolute potential of the calomel electrode; this calculation gave an approximate value of 78 kg.-cal. g.-ion^{-1}.[91] Later work made use of the reasonable hypothesis that entropies of hydration should be proportional to energies of hydration;[94] this approach has led to a hydration energy of 81 kg.-cal. g.-ion^{-1}.[93]

The indefinite significance of the term 'solvation number', and the difficulty of distinguishing between primary (chemical) solvation and secondary (physical) solvation has been emphasised in a review by Bockris.[95] For the bromide ion, for example, values of 0,[96,97] 3·08 (relative to a value of unity for H^+)[98] and 29·6 (5 for H^+)[99] molecules of water per Br^- ion have been suggested. Bockris does not tabulate results for the primary solvation number, n, of Br^-; but data for other ions suggest that n decreases with increasing size of the unhydrated ion, and by interpolation between values for Cl^- and I^-, n for Br^- should be between one and two.

THE BROMIDE-BROMINE STANDARD POTENTIAL

For cells of the type:

$$(+)\text{Pt, KBr}(c) + \text{Br}_2\text{, KBr}(c)\text{, AgBr, Ag}(-)$$

with the concentration of potassium bromide 0·1–1 N. and the bromine concentration from 0·9% to 10·3% of its saturation value, E°_{298} was found to be −0·9940 V.[100] This result was combined with the value $E^\circ_{298} = +0{\cdot}1511$ V. for the cell (−)Ag, AgBr, 0·1 N-KBr ‖ 0·1 N-KCl, AgCl, Ag (+) and the previously determined value for the standard potential of the silver–silver chloride electrode (–0·2223 V.) to give $E^\circ_{298} = -1{\cdot}0652$ V. for the cell:

$$(+)\mathrm{Pt},\ \mathrm{Br_2(liq.)},\ \mathrm{Br^-}\ (a=1)\,||\,\mathrm{H^+}(a=1),\ \mathrm{H_2(1\,atm.)},\ \mathrm{Pt}(-)$$

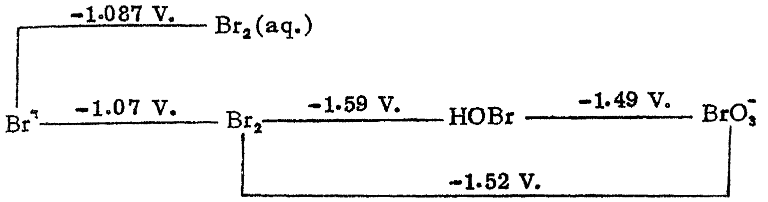
or $E^\circ_{298} = -1{\cdot}0852$ V. for the cell:

$$(+)\mathrm{Pt},\ \mathrm{Br_2}(a=1),\ \mathrm{Br^-}(a=1)\,||\,\mathrm{H^+}(a=1),\ \mathrm{H_2(1\,atm.)},\ \mathrm{Pt}(-)$$

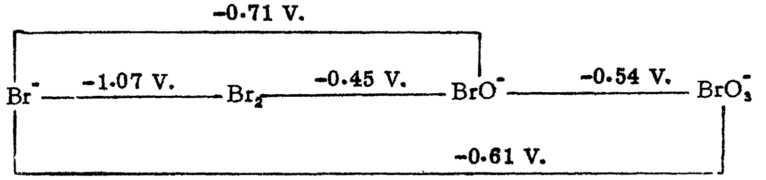
These results agree well with older data (Mellor, II, 65). Their accuracy was confirmed by a cross-checking of the silver–silver bromide electrode against the calomel electrode.[100] The standard potentials for liquid bromine and bromine at unit activity are thus –1·065 V. and –1·085 V. The standard potentials of the system $2\mathrm{Br^-}$ (in solution) = $\mathrm{Br_2}$ (liq.) + $2e$ have been found to be –0·85,[101] –0·79[102] and –1·01 V.[103] in methyl alcohol, and –0·97 V. in ethyl alcohol.[103]

The following summary of the oxidation–reduction chemistry of bromine and its ions is based on that by Latimer,[93] who also discusses the interpretation of such diagrams.

Acidic Solution.



Basic Solution



MAGNETIC PROPERTIES

Pascal's value for the susceptibility of liquid bromine has been confirmed: according to Shur,[149] the specific susceptibilities of both liquid and solid bromine are $-0{\cdot}40 \times 10^{-6}$ c.g.s. units; that of bromine vapour is $-0{\cdot}46 \times 10^{-6}$ c.g.s. units.[148,149] The atomic susceptibility of bromine in organic compounds is given as[104] $30{\cdot}6 \times 10^{-6}$ or[105] $27{\cdot}5 \times 10^{-6}$ c.g.s. units g.atom^{-1}; the latter value is based on only four compounds and is probably of less significance. It has been pointed out that formation of a halogen molecule from atoms should involve a loss in diamagnetic susceptibility.[109]

The susceptibility of the bromide ion in solids has been reported as [106]$34{\cdot}7 \times 10^{-6}$ or [153]$33{\cdot}4 \times 10^{-6}$ c.g.s. units g. ion^{-1}; a value of 39×10^{-6} c.g.s. units g. ion^{-1} has been suggested for the ion in the gaseous state or in solution.[107]

The magnetic rotatory power for light of wave-length 5780 A. is 66×10^{-2} for covalently bound bromine, and 208×10^{-2} for the bromide ion.[108]

DIELECTRIC CONSTANT AND ELECTRICAL CONDUCTIVITY

Two redeterminations of the dielectric constant of liquid bromine gave values of 3·12 at 15° and at a frequency of 187,000 per sec.,[110] and 3·33 at 0° (frequency unspecified).[111] The equation:

$$\varepsilon_t = 3{\cdot}212\ (1 - 0{\cdot}00191t)$$

has been suggested for the variation of ϵ_t with temperature between 1° and 18°,[110] an alternative equation:

$$\epsilon_T = 1{\cdot}0730 + 617{\cdot}4/T$$

has been suggested for the temperature range 0–54°.[111] The dielectric constant of bromine vapour was found to be 1·0047 ± 0·0003 at 760 mm. and 0°; this value was calculated from measurements at 28·5°, at which temperature the constant varied linearly with pressure and was independent of the field strength.[114] The dependence of the constant at higher temperatures on the applied potential was attributed to molecular excitation. Luft confirmed the linear variation of ϵ with pressure at 50–250 mm., and found the dipole moment of bromine vapour to be less than 10^{-19} e.s.u.;[115] the value for liquid bromine is[110] $0{\cdot}40 \times 10^{-18}$ or[111] $0{\cdot}49 \times 10^{-18}$ e.s.u. Theoretical discussions of dielectric constants and physical properties make mention of bromine.[117,118]

Values, tabulated below, for the specific conductivity of liquid bromine vary widely, probably owing to the presence of impurities (the conductivity is greatly increased by traces of water, for example [116]).

TABLE V.- SPECIFIC CONDUCTIVITY OF LIQUID BROMINE

Temp. °C.	$\kappa \times 10^{-10}$	Reference
–9	5·14	
0	6·32	113
0	9·6	110
15·5	8·95	113
18	16	112
25	11·24	113
30	12·63	113

For solid bromine, $\kappa = 0{\cdot}08$ and $0{\cdot}45 \times 10^{-10}$ at –18·5° and –9° respectively.[113]

POLARIZABILITY AND REFRACTIVITY

From a long series of measurements on carefully purified organic compounds, the contributions of a bromine atom to the refractivities for the *C*, *D*, *F* and *G* lines were estimated to be 8·681, 8·741, 8·892 and 9·011; $M_n{}^{20}_{D}$ for bromine was found to be 118·07.[19] These values appear to render obsolete earlier ones[119,150] deduced from relatively small numbers of compounds. The ionic refractivity of the Br^- ion for the *D* line, which is higher than that of covalently bound bromine in compounds, is 12·67;[121] a theoretical treatment gives 12·14.[122] The value 8·62 recorded for light of wave-length 5461 A. appears to be calculated[123] on the erroneous assumption that hydrogen bromide is a polar gas H^+Br^-.

The polarizability of the bromide ion, deduced from data on refractivity, is[125] $4{\cdot}99 \times 10^{-24}$ or[126] $4{\cdot}2 \times 10^{-24}$. For bromine in organic compounds the atomic contribution to the distortion polarization is 8·5.[151] Attention has been directed to the proportionality between refractivity and atomic volume among the halogens;[124] and a theoretical discussion of the dependence of molecular polarizability on ionic size among the halogens has been given.[120]

ATOMIC WEIGHT

Both chemical and physical methods lead to the acceptance for the International Atomic Weight (1951) of 79·916, a value which, despite a number of more recent investigations, has remained unchanged since Baxter's determination of the Ag:AgBr ratio in 1906 (Mellor, II, 106). A determination of the density of pure hydrogen bromide (Mellor, II, 106), after correction for mathematical errors[129] and unfavourable criticism by Baxter[129] was eventually re-evaluated to give Br = 79·918.[132] Hönigschmid and Zintl[130] distilled bromine from calcium bromide solution, reduced it to potassium bromide with halogen-free potassium oxalate, and, while evaporating to crystallize potassium bromide, added a little permanganate from time to time in order to oxidize any iodide present. The potassium bromide was oxidized with somewhat less than the calculated quantity of halogen-free potassium dichromate and sulphuric acid (to avoid liberation of any chlorine), and the bromine, after distillation, was dried over fused calcium oxide and calcium bromide, and was finally distilled in vacuo. A known weight was reduced to bromide by pure ammonium arsenite, and the ratio Br : Ag was determined nephelometrically; the silver bromide was then weighed. The mean of ten determinations of the ratio Br : Ag and nine of the ratio Br : AgBr gave Br = 79·916, the atomic weight of silver being taken as 107·880.[130]

Determination of the Ag : AgBr ratio from head and tail fractions of ammonium bromide subjected to prolonged fractional crystallization failed to reveal any separation of the bromine isotopes.[131] In this work the fractions of ammonium bromide were converted into sodium bromide by heating with sodium carbonate; a little potassium dichromate and sulphuric acid (sufficient to displace about 2% of the total quantity of bromine) were added, and the solution was boiled to remove the liberated bromine and any iodine present. A further quantity of dichromate (equivalent to about 95% of the bromide) was now added, and the bromine was distilled out. The residual solution when treated with dichromate liberated more bromine, showing that excess of broide had been present throughout the distillation of the main fraction of bromine. After reduction with dilute aqueous ammonia, the ratio Ag : AgBr was determined by adding a dilute aqueous solution of silver nitrate (made from a known weight of silver), and washing, drying first at 85–90° and then at 250–300°, and weighing the silver bromide formed. The agreement between the mean result Br = 79·914 and other accurate determinations shows the value of the very much shorter process for the purification of bromine used in this work; economy in material is another considerable advantage.

Fractional condensation of solid bromine from the vapour also failed to effect any separation of the isotopes of bromine; the most volatile fraction had Br = 79·916, compared with Br = 79·915 (both from Ag : AgBr) on the starting material.[133] Determination of the ratios $KBrO_3$: KBr and KBr : Ag gave Ag = 107·879, which, when combined with Hönigschmid and Zintl's value for Ag : Br,[130] yielded Br = 79·915 for the atomic weight of bromine.[134]

Bromine was one of the first elements to be investigated in the mass spectrograph, and Aston[127] found it to be a mixture of approximately equal parts of isotopes of mass number 79 and 81. A later determination by the same author gave Br = 79·916 ± 0·002 on the chemical scale; the physical isotopic weights were determined as 78·929 and 80·926, with an abundance ratio of unity.[135] Blewett, using a Dempster-type mass spectrograph, found no evidence for a third isotopic constituent in ordinary bromine; he estimated the sensitivity of his determination as 1 in 3000.[81] The abundance ratio of ^{81}Br : ^{79}Br was found to be 0·975 ± 0·025, giving a chemical atomic weight Br = 79·90 ± 0·02.[81]

The theory of the separation of the bromine isotopes by thermal diffusion[138] and exchange reactions[136,137] has been discussed; the calculated equilibrium constants for exchange reactions involving these isotopes are very little removed from unity, and the possibility of any considerable separation appears remote.[137]

MISCELLANEOUS PHYSICAL PROPERTIES

Bromine vapour gives a positive Joshi effect (decrease in conductivity in an alternating electric field when the vapour is exposed to light) at low potentials, and a negative effect at high potentials.[139-141] Mixtures of bromine and hydrogen are reported to produce effects proportional to the concentrations of the gases.[141]

The thermal conductivity of bromine vapour is independent of pressure at pressures greater than 2 mm., but its magnitude has not been measured.[174] The rates of diffusion of bromine into hydrogen, nitrogen, oxygen and carbon dioxide have been studied using the colour of bromine as an indicator: the respective diffusion coefficients are 0·598, 0·132, 0·133 and 0·107.[145] Glass is impermeable to bromine under ordinary conditions; and even during 9·5 years (including 100 days at 360°) no bromine was found to diffuse through tubes with walls 0·21 mm. thick.[266]

Other subjects of minor chemical interest on which information has been given are: the effect of bromine on the viscosity of sulphur,[336] on the temperature coefficient of the resistance of selenium,[337] and on the mobility of ions in hydrogen and in oxygen,[142] the thermionic emission of platinum in bromine;[338] a possible connection between the velocity of sound in bromine and its chemical reactivity;[143] and the relationship of velocity of sound in organic liquids, of known molecular weight and density, to chemical constitution.[144]

THE DISSOCIATION OF BROMINE AND THE RECOMBINATION OF BROMINE ATOMS

The thermal dissociation of bromine into atoms becomes measurable at about 650°. From the data of Bodenstein and Cramer (Mellor, II, 48) for the degree of dissociation and the equilibrium constant between 800° and 1284°, the heat of dissociation has been calculated to be 46·8 kg.-cal. at -273°,[166] 47·0 kg.-cal. at -7°,[164] 47·1 kg.-cal. at 59°,[165] and 48·5 kg.-cal. at 1044°.[165] Other values for the dissociation constant have been obtained by measurement of the vapour pressure of bromine at 650–900° by an adaptation of Knudsen's method: at 650° and 900° $\log K_p = -5{\cdot}98$ and $-3{\cdot}98$ respectively.[167] The latter value is much lower than those of Bodenstein and Cramer for 877° and 936°; they found $\log K_p = -3{\cdot}37$ and $-2{\cdot}89$ at these temperatures.

Gaydon, in a review of the determination of the dissociation energy from the convergence limit of the ultra-violet spectrum, gives 45·44 kg.-cal. for the heat of dissociation into normal atoms.[168] The slightly different Bureau of Standards' value for ΔH° for the monatomic gas has been given with other thermodynamic properties of bromine (see page 699).

It is now generally believed that the Budde effect (Mellor, II, 63) is due to photochemical dissociation of a halogen molecule, followed by recombination of the atoms with liberation of heat and consequent expansion of the vapour. When the Budde effect was first observed for bromine, it was reported that presence of a trace of water was essential for observation of the effect.[170] Later work was reported to show that the magnitude of the effect was proportional to the partial pressures of bromine and water vapour, and was a maximum for light of wave-length 5500 A.; for moist bromine vapour light of wave-length greater than 5800 A. produced no effect. This was attributed to the intermediate formation of an unstable hydrate of formula Br_2,H_2O, which dissociated into two atoms of bromine and a molecule of water.[171] The catalytic effect of water was further substantiated by the observation that the beginning of the region of marked absorption by bromine is moved from 5700 A. for the dry gas to 6110 A. for the wet gas, corresponding to a decrease in the activation energy of dissociation of 3·12 kg.-cal.[171] Unfortunately other authors have failed completely to confirm some of these data. Brown and Chapman, using a gas-filled tungsten filament lamp and filtering the light through ferrous ammonium sulphate or sodium dichromate solution, found that drying bromine over phosphorus pentoxide for several months did not diminish the Budde effect;[172] their conclusions were confirmed by Kistiakowsky,[173] and, later, by Smith, Ritchie, and Ludlam.[174] On the other hand, Matthews found that drying bromine vapour over phosphorus pentoxide for eight weeks decreased, but did not destroy, the effect.[169] He also found that the magnitude of the effect was increased by the presence of air; more extensive investigations on the effect of foreign gases in facilitating the homogeneous recombination of bromine atoms gave the following sequence for decreasing efficiency: CO_2, O_2, N_2, H_2, A.[174] This result agrees with observations of other workers on this reaction (see below). The most recent experiments appear to establish that traces of moisture are without effect.[174]

Bromine atoms have also been produced by the action of an electric discharge in the vapour at 0·1 mm. pressure; their mean life has been estimated at $1{\cdot}8 \times 10^{-3}$ sec., recombination occurring on the wall of the tube.[175] The photochemical production of bromine atoms and their combination have been more thoroughly studied. Bodenstein and Lütkemeyer,[176] in a pioneer study of reactions between free atoms, compared the rates of the hydrogen–bromine reaction in the dark and in light from a tungsten arc lamp in the temperature range 160–218°. Under both sets of conditions, the stationary concentration of bromine atoms determines the rate of formation of hydrogen bromide; this rate is thus an indicator for the concentration of bromine atoms. Knowing the concentration in the dark reaction from the concentration of molecular bromine and its degree of dissociation, the concentration of bromine atoms in the photochemical reaction is obtained; the rate of formation of atoms, estimated by assuming Einstein's law of photochemical equivalence, must in the stationary state be equal to the rate of recombination. By this method, it was found that about one collision in a thousand between bromine atoms leads to the formation of a molecule,[176,183] For the reverse reaction, Bodenstein reported that at 300° and 1 atm. about one impact of molecules in 120 results in the formation of atoms; at 218° and 0·3–0·8 atm. in light, about one impact in 500 is effective.[177] The rate of formation of bromine atoms from molecules was at first believed to be faster than could be accounted for on the basis of activation by collision, but later calculations show that this is not necessarily so.[178-182]

The Budde effect and the hydrogen–bromine reaction, as sources of information on the recombination of bromine atoms, are rather complicated. It has been established by spectroscopy that direct recombination of two atoms in the absence of a third body is a very rare event;[190-192] most of the latest experimental work on the reaction has been concerned with the effect of different gases in facilitating recombination.

Rabinowitch and his co-workers[184-186] studied the dissociation by measuring the change in the molecular absorption coefficient of illuminated bromine vapour. From such measurements they evaluated the equilibrium constant of the reaction $Br_2 \rightleftharpoons 2Br$ and, since the velocity of decomposition may be found from the number of quanta absorbed, the recombination velocity may be calculated. Thermal disturbances were found to be a minimum when the reaction was investigated in helium. The velocity of homogeneous recombination was found to be inversely proportional to the square root of the pressure, in accordance with the recombination mechanism

$$Br + Br + He \rightarrow Br_2 + He$$

The velocity constant was found to be $7{\cdot}5 \times 10^{-33}$ (concentrations in molecules per c.c.). This corresponds to one double collision between bromine atoms in 1100 being a combining collision, or to practically every triple collision being effective.[184,185] The effect of the added gas in promoting recombination increases along the series He, A, N_2, O_2, CH_4 and CO_2; in the last gas, about one double collision in 175 is a recombining one.[185] This order is in general agreement with that deduced from the study of the hydrogen–bromine reaction.[187] These results have been discussed in theoretical reviews of atom combination reactions.[186,188,189]

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THE HYDROGEN-BROMINE REACTION

The kinetics of this reaction have been examined by a large number of investigators.[176,197–207,340] The following account is based largely on the the review by Semenoff,[193] with the inclusion of later work published after that review was written.

The kinetics of the thermal reaction can be represented by the equation:

$$\frac{d}{dt}[\mathrm{HBr}]_t = \frac{2k_t[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{1+[\mathrm{HBr}]/10[\mathrm{Br_2}]}$$

in the temperature range 228–302°; the activation energy of the reaction $H_2 + Br_2 = 2HBr$ is about 40 kg.-cal.; the first stage in the reaction is dissociation of bromine molecules into atoms.

The photochemical reaction also proceeds via the dissociation of a bromine molecule into atoms.[176] At room temperature the quantum yield for the overall reaction is far below unity; in the temperature range 160–210° it increases about 1·5 times for each 10° rise in temperature. Here, the rate of formation of hydrogen bromide is given by the equation

$$\frac{d}{dt}[\mathrm{HBr}]_p = 2K_p\, I_{\mathrm{abs.}}^{1/2}\cdot\ \frac{[\mathrm{H_2}]}{1+[\mathrm{HBr}]/10[\mathrm{Br_2}]}$$

where $I_{\mathrm{abs.}}$ is the number of quanta absorbed by the bromine; and if I = the number of incident quanta and α = absorption coefficient of bromine,

$$I_{\mathrm{abs.}} = \alpha I[\mathrm{Br_2}]$$

Substitution in the equation for the rate of the photochemical reaction gives:

$$\frac{d}{dt}[\mathrm{HBr}]_p = 2K_p'\,\frac{[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{1+[\mathrm{HBr}]/10[\mathrm{Br_2}]}$$

These experimental results have been interpreted by the following reaction scheme:[194–196]

$$\begin{array}{llr}
\mathrm{Br_2} \xrightarrow{k_1} \mathrm{2Br} & & (1)\\
\mathrm{Br + H_2} \xrightarrow{k_2} \mathrm{HBr + H} & & (2)\\
\mathrm{H + Br_2} \xrightarrow{k_3} \mathrm{HBr + Br} & & (3)\\
\mathrm{H + HBr} \xrightarrow{k_4} \mathrm{H_2 + Br} & & (4)\\
\mathrm{Br + Br} \xrightarrow{k_5} \mathrm{Br_2} & & (5)
\end{array}$$

Since reaction (2) is endothermic to the extent of 16·4 kg.-cal., most collisions between bromine atoms and hydrogen molecules will not lead to reaction at ordinary temperatures; at higher temperatures the probability of reaction is greatly increased – hence the variation of the quantum yield of the overall reaction with temperature. When a steady state is reached, the concentration of intermediate products is taken as constant. This leads, for the thermal reaction, to the equation:

$$\frac{d}{dt}[\mathrm{HBr}]_t = 2k_2\left(\frac{k_1}{k_5}\right)^{1/2}\frac{[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{1+\dfrac{k_4}{k_3}\dfrac{[\mathrm{HBr}]}{[\mathrm{Br_2}]}}$$

By substituting $k_t = k_2\sqrt{k_1/k_5}$ and $k_4/k_3 = 0{\cdot}1$, the expression for the experimental results is obtained. A similar treatment of the photochemical reaction leads to the equation:

$$\frac{d}{dt}[HBr]_p = \frac{2K_p [H_2]\, I^{1/2}_{abs.}}{1 + \frac{k_4[HBr]}{k_3[Br_2]}}$$

where $K_p = k_2/\sqrt{k_5}$ for this reaction. Since the ratio k_1/k_5 is the known equilibrium constant for the dissociation of bromine, k_2 may be obtained from the experimentally determined value of k_t for a given temperature. From values of k_2, the activation energy for (2) is 17·6 kg.-cal.: since reaction (2) is endothermic (16·4 kg.-cal.) the activation energy for reaction (4) must be 1·2 kg.-cal. Since k_3/k_4 is found experimentally to be independent of temperature, the activation energy of (3) must also be about 1·2 kg.-cal. From the calculated rate of (5) and the equilibrium constant for the dissociation of bromine, k_1 can be shown to be expressed very roughly by the equation:

$$k_1 = 10^{13} \times e^{-45{,}200/RT}$$

the activation energy of 45·2 kg.-cal. being equal to the heat of dissociation of bromine. There is, however, the effect of a third body on the dissociation of bromine to be considered; and since k_1 will therefore show some variation with pressure, the rate of the overall hydrogen–bromine reaction shows a similar slight variation.[197,198]

In the presence of nitric oxide, the rate of the photochemical reaction becomes proportional to the intensity of the light.[205] Comparison of the rates of reaction of hydrogen and deuterium with bromine gives 17·2 ± 0·5 and 19·3 ± 0·5 kg.-cal. for the activation energies of reaction (2) and the analogous reaction involving deuterium.[207] Investigations have also been made on the influence of the walls of the reaction vessel,[197,206] the effect of higher temperatures,[201] the presence of water vapour[199,200] or inert gases,[204] and the wave-length of light used in the photochemical reaction.[201,202] A number of theoretical discussions have also been given.[208-213]

The effect of pressure on the explosion temperature of mixtures of hydrogen and bromine has been investigated.[214-216] For x% of bromine, a total pressure P mm. and a temperature T at which detonation occurs the following relationships hold. For a constant value of x, between 680° and 870° K. and 17·5 and 300 mm.,

$$\log (P/T) = \text{const.} + 4000/T.$$

At a constant temperature, P is minimal when $x \sim 67\%$. Increase in the diameter of the reaction vessel decreases T by increasing the chain length. Addition of nitrogen increases T, addition of hydrogen bromide has little effect. Coating the surface with potassium chloride decreases T. The effect of x on P at a given temperature is attributed to the effect of composition on the thermal conductivity of the mixture; the reaction mechanism under these conditions has not, however, been investigated in any detail.

EXCHANGE REACTIONS INVOLVING BROMINE ISOTOPES

The observation that the exchange reaction:

$$HBr^* + BrBr \rightleftharpoons HBr + Br^*Br$$

in the gas phase (using the ^{80}Br and ^{82}Br isotopes as indicators) attains equilibrium in 2 min. at room temperature was at first attributed to a chain reaction involving bromine atoms.[250] Libby, however, suggested that the main reaction proceeds through the formation of a complex of formula HBr_3;[251] and by demonstrating that fluorine and hydrogen fluoride show no similar rapid exchange, he claimed to have provided indirect evidence for the correctness of his suggestion.[252]

Later work by Jacobson, using ^{82}Br, established that the half-life of the exchange reaction at room temperature under a pressure of approx. 1 mm. of mercury was 0·14–0·75 sec.; this time was reduced to 0·06–0·08 sec. when the mixing chamber was packed with silica wool.[253] Furthermore, he found no evidence of a photochemical effect. The main reaction thus appears to proceed heterogeneously, but the mechanism remains uncertain.

Freshly coagulated silver bromide exchanges its bromine with potassium bromide solution rapidly at first (10% exchange in 1 min.) then much more slowly as the precipitate ages.[254] Bromine dissolved in a dilute solution of potassium bromide exchanges rapidly with all of the bromine in the $PtBr_4^{--}$ and $PtBr_6^{--}$ ions in aqueous solution.[255] Interchange of radiobromine between the $PtBr_4^{--}$ and $PtBr_2$ ions and the non-ionic complex $Pt(NH_3)_2Bt_2$ also proceeds readily.[256] Lead bromide exchanges with radiobromine dissolved in potassium bromide solution, and this has been interpreted as indicating formation of complex ions $PbBr_3^-$ and $PbBr_4^{--}$;[257] the evidence cited in support of this conclusion is scanty.

In the temperature range 170–200° exchange between radiobromine and carbon tetrabromide vapour is homogeneous and proceeds at a rate proportional to the first power of the cencentration of the carbon tetrabromide and the square root of the concentration of the bromine.[258] This strongly suggests that the mechanism is:

$$CBr_4 + Br^* \rightarrow CBr_3 + BrBr^*$$

$$CBr_3 + BrBr^* \rightarrow CBr_3Br^* + Br$$

In the liquid phase, between 107° and 160°, the reaction proceeds by the same route, with an activation energy of 3 kg.-cal.[258] Bromine in carbon tetrachloride at room temperature exchanges rapidly with arsenic tribromide or stannic bromide, but not with ethylene dibromide or bromotrichloromethane; with the latter, there is no exchange in the dark at 100°, but a rapid exchange occurs at 76° in green light.[257] The mechanism of this last reaction is presumably similar to that given above for the bromine-carbon tetrabromide exchange. Antimony tribromide[260] and selenium tetrabromide[261] also exchange with radiobromine in less than 1 hr. at 50° in carbon disulphide. In the formation of higher bromides from cuprous bromide, aurous bromide, or phosphorus tribromide and bromine containing ^{81}Br, the bromine atoms in the products have been shown to be equivalent in each instance.[262] (See also Chapter V).

SOLUTIONS IN WATER AND AQUEOUS SOLUTIONS OF BROMIDES

The total solubility of bromine in water at 25° is 0·2141 mole per litre, but owing to the hydrolysis and the interaction of the bromide ions produced with more bromine this figure is a composite one: the concentration of molecular bromine in such a solution is 0·2098 mole per litre.[217] The hydrolysis constant of bromine, determined from conductivity measurements, is $0{\cdot}70 \times 10^{-9}$ at 0°,[218] $1{\cdot}78 \times 10^{-9}$ at 10°,[218] $5{\cdot}8 \times 10^{-9}$ at 25°,[217,218] $8{\cdot}3 \times 10^{-9}$ at 30°,[218] and $11{\cdot}3 \times 10^{-9}$ at 350°.[218] Measurement of the pH of bromine solutions with the glass electrode indicates a value of $4{\cdot}2 \times 10^{-9}$ at 25°.[219] Interpretation of these results is complicated by the different importance of the equilibria

$$Br^- + Br_2 \rightleftharpoons Br_3^- \qquad \text{and} \qquad Br_3^- + Br_2 \rightleftharpoons Br_5^-$$

at different temperatures, lower temperatures favouring polybromide ion formation.[218,220] The vapour pressure of bromine above its 0·1 N. solution in water is 18·8 mm. at 12°; above a similar solution in N-potassium bromide it is only 1·7 mm., and in 6 N-hydrochloric acid, 3·0 mm.[221] According to Jander and Feit,[222] the presence of calcium chloride in solution increases the volatility, whilst the presence of sodium chloride, hydrochloric acid or potassium bromide decreases it; such a difference between two chlorides in aqueous solution would be remarkable and obviously needs confirmation. Bromine water in equilibrium with liquid bromine (saturated with water) has a v.p. of 748·8 mm. at 53·6°; at this temperature the aqueous layer contains 3·50 g. of bromine per 100 g., and the vapour evolved contains 98·8 g. of bromine per 100 g.[223] The first product in the photochemical reaction between bromine and water is believed to be hypobromous acid, which then decomposes giving hydrobromic acid and oxygen.[224] The decrease in the rate produced by addition of bromide ions is due to formation of polyhalide ions.

Early work on bromine hydrate (Mellor, II, 73) appeared to indicate a formula $Br_2,10H_2O$, and this formula was supported by Harris.[225,231] On the other hand d'Ans and Höfer, from their study of the Br_2-H_2O system, reported the formula $Br_2,8H_2O$;[226] their value for the transition point for the system

$$Br_2,8H_2O(s) = Br_2(liq.) + 8H_2O(liq.)$$

of 5·8°, however, is almost the same as that reported earlier (6·2°) for the system involving the decahydrate. The most likely interpretation of these results appears to be that the decahydrate represents only partial formation of the hydrate of ideal composition $Br_2,8H_2O$. The unit cell of bromine hydrate has been shown to contain $48H_2O$, like that of sulphur dioxide (which has been studied in much more detail); the structure is probably that of a form of ice with bromine molecules occupying cavities in a relatively open structure.[228] This structure has not yet received a full experimental confirmation, however. The heat of formation of bromine hydrate has been calculated from Roozeboom's values for the dissociation pressure: $\Delta H = 7{\cdot}9$ kg.-cal. for the reaction[341]

$$Br_2,10H_2O_{(s)} = Br_{2(g)} + 10H_2O_{(s)}$$

From a study of the distribution of bromine between water and potassium bromide solutions, using the Jones and Kaplan equilibrator,[227] the equilibrium constants of the reactions

$$Br^- + Br_2 \rightleftharpoons Br_3^-$$
$$Br^- + 2Br_2 \rightleftharpoons Br_5^-$$

in solution were found to be 16 and 40 respectively at 25°. From the distribution of bromine between carbon tetrachloride and aqueous solutions of hydrobromic acid, K for the formation of the Br_3^- ion was found to increase from 16·8 in 0·1 M-acid to 17·6 in 0·52 M-acid.[236] Similar investigations on the partition between carbon tetrachloride and solutions of hydrobromic acid and lithium, sodium, and potassium bromides at 21·5°, and between carbon tetrachloride and solutions of sodium and potassium bromide at 16·5°, also show that K varies slightly with the ionic strength of the solution. The mean value for K at zero ionic strength is 17·4 at 21·5° and 18·4 at 16·5°.[233]

The solubility of bromine in strontium bromide solutions has been measured and Table VI shows some of the results:[229]

TABLE VI.- SOLUBILITY OF BROMINE IN STRONTIUM BROMIDE SOLUTIONS

Concn. $SrBr_2$ moles/1000 g.H_2O	0·0000	0·02455	0·0618	0·1992	0·3911
Concn. Br_2 moles/1000 g.H_2O	0·2197	0·2653	0·3487	0·7359	1·259

These results, like those for the solubility in potassium bromide solutions (Mellor, II, 83) indicate formation of Br_5^- as well as Br_3^- ions. The solubilities of bromine in 1·070, 2·140 and 3·106 M-hydrochloric acid are 0·496, 0·816 and 1·164 moles Br_2/litre at 20·8°; those in 0·104, 0·416 and 1·664 M-hydrobromic acid at the same temperature are 0·333, 0·681 and 2·129 moles Br_2/litre respectively.[233] The solubilities in 0·701, 1·387 and 2·313 M-sodium chloride solutions at 20·6° are 0·321, 0·425 and 0·612 moles Br_2/litre.[233]

In the tetramethylammonium bromide system, $(CH_3)_4NBr$-Br_2, the compounds

$(CH_3)_4NBr_3$ (m.p. 118·5°)[234,235] and $(CH_3)_4NBr_9$ (m.p. 56·7°)[234] have been reported. The only alkali metal polybromide which has been obtained in the anhydrous state is caesium tribromide.[231] None of these substances has been investigated by *X*-ray diffraction, and there is no information on the structures of the polybromide ions.

The ionic mobilities of the Br_3^- and Br_5^- ions at 25°, determined from conductivity measurements, are 43 and 30 ohm^{-1}cm^{-1} respectively. The acid present in the solution of bromine in hydrobromic acid appears to be a very strong one;[230] this may be correlated with the failure to prepare the anhydrous acid HBr_3 or other similar acids of which polyhalides are salts.

SOLUTIONS IN NON-AQUEOUS SOLVENTS

Bromine is miscible in all proportions with chloroform or carbon tetrachloride. Bromine and chloroform form a eutectic containing 17 mole % Br_2 (m.p. −72°), but form no compounds.[239,242] This observation is in accord with the relative reactivities of bromine and chlorine in chloroform towards sodium: chlorine, which does form additive compounds, reacts less rapidly than bromine.[239] Bromine and carbon tetrachloride form a eutectic containing 25 mole % Br_2 (m.p. −44°)[240] and an azeotrope containing a mole fraction of 0·884 of bromine (b.p. 57·7° at 735·6 mm.).[241] The specific gravity of the azeotrope is 4% less than that calculated assuming the solution to be ideal; this is attributed to the large difference between the internal pressures of bromine and carbon tetrachloride (5700 and 3070 atm. respectively[237]). Freezing-point curves fail to reveal any evidence for compound formation in systems involving bromine and the following substances: boron tribromide,[320] carbon tetrabromide,[243] silicon tetrabromide,[240] titanium tetrabromide,[240] stannic bromide,[240] arsenic tribromide,[240] and antimony tribromide.[240] Bromine and phosphorus trichloride yield mixtures of inadequately characterized chlorobromides.[333-335]

Bromine is readily soluble in ethyl ether, and the compounds $(C_2H_5)_2O,Br_2$ and $(C_2H_5)_2O,Br_3$ are reported in the earlier literature. Above −40°, however, interaction of bromine and ether, with liberation of hydrogen bromide, takes place slowly; and McIntosh, in his study of the bromine–ether system, was unable to prepare the tribromide free from hydrogen bromide.[244] This, he pointed out, may mean that the formula of the tribromide is really $[(C_2H_5)_2OH]^+Br_3^-$ (writing it as an oxonium salt), and that the conductivity of ethereal solutions of bromine is due to this substance. Bruns measured the conductivity of mixtures of bromine and other ethers, dried over phosphorus pentoxide, with the following results:[245]

TABLE VII.- ELECTRICAL CONDUCTIVITY OF MIXTURES OF BROMINE WITH ETHERS

% by wt. di-*n*-propyl ether	2·5	4·8	7·1	10·5	18·5
$10^3\kappa$ at 0° ohm^{-1} cm^{-1}	1·49	4·82	12·8	13·8	12·6
% by wt. di-*iso*amyl ether	18·3	23·2			
$10^3\kappa$ at 0°	1·87	1·97			
% by wt. dimethyl ether	5·2	10·5	14·8	21·4	28·4
$10^6\kappa$ at −70°	3·00	4·28	8·26	8·28	6·68

The temperature variation of the conductivity of the 5·2% solution in dimethyl ether was:[245]

t	−70°	−50°	−34°	−18°	−13°
$10^6\kappa$	3·00	4·51	6·09	8·06	8·76

On electrolysis of the solution in diethyl ether, bromine is deposited on a silver anode in accordance with Faraday's Law.[245] Bruns rejected McIntosh's explanation of the conductivity, but his decision should not be regarded as final; dissociation of the type he suggests, into $(C_2H_5)_2O^{3+}$ and Br^- ions, does not appear very probable in a medium of low dielectric constant.

Systems involving nitrogen-containing organic compounds (pyridine,[246,247] quinoline,[246] acetamide[263] and benzamide[248,249]) and bromine have also been investigated. The conductivity of the bromine-pyridine system is a maximum at 9 mole % of pyridine and has a positive temperature coefficient; dissociation is believed to proceed according to the equation:

$$C_3H_5NBr_n \rightleftharpoons C_5H_5NBr^+_{n-1} + Br^-$$

The variation in the conductivity of mixtures of bromine and quinoline with time strongly suggests that reaction occurs, and the significance of this is doubtful. Bromine and benzamide form a red additive compound $C_6H_5CONH_2,Br_2$ which appears to dissociate in bromine,[248] but again the conductivity varies with time and its interpretation is obscure. An analogous addition product is formed from acetamide and bromine.[263]

Bromine is miscible with liquid sulphur dioxide in all proportions.[264] The report[265] that bromine undergoes dissociation (shown cryoscopically) in liquid chlorine, although the solution is a non-conductor, can readily be accounted for by the formation of undissociated molecules of bromine chloride:

$$Br_2 + Cl_2 \rightleftharpoons 2BrCl$$

The vapour pressure of bromine above its saturated solution in glacial acetic acid is only 0·26 mm.;[221] the nature of the solution, however, has not been studied.

ADSORPTION OF BROMINE

The amount of bromine which can be adsorbed on silica gel is dependent on the method of preparation of the gel.[267] Adsorption at room temperature is, however, accompanied by condensation phenomena, and the size of the pores of the gel determines how much bromine is taken up. The adsorption by silica gel in the temperature range 58° to 138° has been studied in some detail.[268] The silica gel was washed with nitric acid and water, and after being electro-dialyzed for two days was dried and air-activated at 600°. Typical results are given in Table VIII.

TABLE VIII.–ADSORPTION OF BROMINE BY SILICA GEL.

(a) 58·0° p(mm.)	3·7	16·1	38·2	88·6	239·0
millimoles per g. silica gel	0·0384	0·1238	0·2585	0·551	1·891
(b) 79·0° p(mm.)	11·5	69·8	218·6	395·4	756·0
millimoles per g. silica gel	0·0473	0·2342	0·6911	1·410	4·648
(c) 99·9° p(mm.)	12·9	72·6	151·3	392·6	744·4
millimoles per g. silica gel	0·0267	0·1443	0·2770	0·682	1·450
(d) 117·5° p(mm.)	67·7	139·4	174·2	392·0	790·4
millimoles per g. silica gel	0·0809	0·1585	0·1889	0·4076	0·831
(e) 137·7° p(mm.)	68·1	139·5	173·3	393·8	789·8
millimoles per g. silica gel	0·0570	0·1039	0·1297	0·2663	0·521

These results do not fit either the classical or the Langmuir adsorption isotherm, and appear to indicate loose physical binding or capillary condensation.[238] A partial investigation of the magnetic susceptibility of the bromine-silica gel system, however, has shown that the susceptibility is not an additive function of the susceptibilities of the components.[269]

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The validity of early investigations of the adsorption of bromine from aqueous solutions by charcoal has been challenged by Kolthoff,[272] who has drawn attention to an observation of Freundlich that bromine water is decomposed in the presence of charcoal. Kolthoff found the main reaction to be:

$$2Br_2 + 2H_2O \rightarrow 4HBr + O_2$$

Bromine in carbon tetrachloride solution is not decomposed, and adsorption from this solvent or from chloroform (or from mixtures of these solvents) accurately obeys the so-called Freundlich equation.[270,271] Removal of the adsorbed bromine is difficult, a temperature exceeding 400° being required for complete desorption in a reasonable time.[273]

Adsorption from the vapour phase by steam-activated charcoal previously degassed at 700° has been measured, and the results[238,274] are given in Table IX.

TABLE IX.- ADSORPTION OF BROMINE BY CHARCOAL

(a) 58·0° *p*(mm.)	3·0	11·4	68·8	140·4	265·7	473·0	691·8
millimoles Br per g. C.	4·607	4·972	5·358	5·554	5·665	5·779	5·849
(b) 98·1° *p*(mm.)	3·0	18·6	68·3	266·2	792·3		
millimoles Br per g. C.	3·044	4·729	5·048	5·311	5·527		
(c) 137·6° *p*(mm.)	1·8	19·2	68·1	265·8	791·5		
millimoles Br per g. C.	3·355	4·207	4·629	4·990	5·217		
(d) 178·4° *p*(mm.)	3·0	16·8	67·2	266·8	787·8		
millimoles Br per g. C.	3·016	3·619	4·413	4·628	4·899		

The rate of adsorption was investigated at 137·6°C. and at pressures varying between 0·03 mm. and 791·5 mm.; equilibrium was found to be reached in about fifteen hours under these conditions.[274] The average value, calculated from these results, for the differential heat of adsorption of bromine on charcoal was 11·4 kg.-cal. per mole of bromine, this value being about 4 kg.-cal. greater than the latent heat of evaporation.[238]

The nature of adsorption of bromine by carbon has been investigated. At room temperature the limiting composition of the product formed from graphite and bromine vapour is C_8Br; *X*-ray analysis by the powder method shows that each bromine layer is separated by two layers of carbon atoms from the next bromine layer, with the C–Br–C distance 7·05 A. and the C–C interlayer distance 3·35 A.[276] Since, by comparison with carbon monofluoride, graphite bromide is relatively unstable, it has usually been assumed that the bromine enters the structure in the form of Br_2 molecules. The C–C distances within layers of carbon atoms might throw light on the structure by showing whether the C–C bond order is less than that in pure graphite, but unfortunately they are not yet available. Adsorption of bromine greatly increases the electrical conductivity of active charcoal, the effect being proportional to the external pressure exerted on the charcoal.[275] The magnetic susceptibility of bromine-charcoal has been known for some time to differ from the value calculated for a mixture of bromine and graphite,[269,277,278] and a careful study of the system has recently been made by Goldsmith.[279] At 298°K. the susceptibility of graphite is $-5{\cdot}3 \times 10^{-6}$ c.g.s. units $g.^{-1}$; at 75°K. it is $-7{\cdot}4 \times 10^{-6}$ c.g.s. units $g.^{-1}$. For bromine-graphite samples the following values were obtained:

g.Br/g.C	$\chi \times 10^6$ 298°K	 75°K.
0·051	–4·2	–5·4
0·67	–0·31	–0·29
0·71	–0·31	–0·29

These values are incompatible with the occurrence of the whole of the bromine as atoms or as molecules; they appear to require the presence of a few carbon-bromine bonds.[279]

'POSITIVE' BROMINE

In organic chemistry, bromine atoms (e.g., in N-bromoamides) which in the presence of ammonia, alcoholic alkali, or halogen acids are replaced by hydrogen are usually called 'positive'. Waters[280] and Altschul and Bartlett,[281] however, have concluded that there is no sharp distinction between such halogens and others, and Waters has advanced strong arguments for the view that bond fission in 'positive' bromine compounds is often a homolytic process. The term 'positive bromine' is therefore restricted here to a free or solvated bromine cation.

In mineral acid (though not in neutral) solution in the absence of bromide, hypobromous acid is a much more powerful brominating agent than bromine, converting benzene into bromobenzene very rapidly at room temperature. By treating bromine water with a salt of silver or other metal which forms an insoluble bromide, a solution of similar brominating power is obtained.[282] These observations are interpreted as showing the formation of bromine cations by the reactions:

$$HOBr + H^+ \rightleftharpoons Br.H_2O^+$$

$$Br_2 + Ag^+_{(aq)} \rightarrow AgBr + Br^+_{(aq)}$$

The thermochemistry of the process

$$Br_2 + H_2O \rightleftharpoons Br.H_2O^+ + Br^-$$

in aqueous solution has been discussed theoretically by Bell and Gelles,[342] who estimate the equilibrium constant for this reaction as about 10^{-20}, a value which is compatible with the presence of small concentrations of solvated bromine cations in solution. Further evidence for the existence of such cations has been provided by the observation that on electrodialysis through a collodion-impregnated membrane bromine can be isolated from a 4% solution of hypobromous acid in the presence of 7% of sulphuric acid.[283]

Some stable compounds in which a bromine cation appears to be stabilized by co-ordination with pyridine are known. Silver nitrate (3 g.) dissolved in a mixture of dry pyridine (5 c.c.) and chloroform (10 c.c.) reacts with bromine (3 g. in 10 c.c. of chloroform) to form silver bromide and a solution from which petroleum ether precipitates the white crystalline hygroscopic compound $Br(C_5H_5N)_2.NO_3$ (m.p. 78°).[284] This substance is soluble in chloroform or pyridine but insoluble in carbon tetrachloride; it is very reactive, and with *cyclo*hexene, for example, gives the saturated product $C_6H_{10}BrNO_3$.[284] An alternative precipitant for the nitrate is diethyl ether; and from silver perchlorate, pyridine and bromine in chloroform the perchlorate $Br(C_5H_5N)_2ClO_4$ may be obtained by similar methods.[343]

The bromine pyridinium nitrate on treatment with aqueous 0·4 N-sodium hydroxide yields a yellow precipitate which when rapidly dried on a porous plate and then in vacuo over solid potassium hydroxide has the empirical composition Br_2O,H_2O,C_5H_5N.[344] The constitution $(Br,H_2O,C_5H_5N)^+ OBr^-$ has been suggested for this substance;[344] but no work on its structure has been reported.

The interaction of bromine and the silver salts of perchloric or trifluoroacetic acids in the presence of aromatic compounds results in bromination of the aromatic compound in the position to be expected for electrophilic attack: bromine, silver perchlorate or trifluoroacetate and benzoic acid, for example, yield *m*-bromobenzoic acid; toluene is converted into p-bromotoluene.[345-347] This strongly suggests that free or solvated Br^+ ions participate in such halogenations.

MISCELLANEOUS CHEMICAL PROPERTIES OF BROMINE

The interaction of bromine and hydrogen is discussed from the point of view of mechanism on page 706 and in connexion with the preparation of hydrogen bromide on page 724. As might be expected, bromine reacts very rapidly with previously prepared atomic hydrogen:[285,286]

$$H + Br_2 \rightarrow HBr + Br$$

Bromine will not react with molecular oxygen, but by the action of atomic oxygen or ozone on bromine under suitable conditions, bromine oxides (see page 748) have been prepared. The formation of the oxide Br_3O_8 probably accounts for the action of bromine as a sensitizer for the photochemical decomposition of ozone by a mechanism similar to that established for the decomposition of ozone in the presence of chlorine, the quantum efficiency of 30 with light of wave-length 5460 or 3650 A. for the bromine-sensitized decomposition indicates a chain reaction in which the decomposition products of the oxide react with more ozone.[287,288] Bromine also sensitizes the photo-decomposition of chlorine dioxide by light of wave-length 5460 A., the quantum yield being the same as that in the reaction induced by light of wave-length 3650 A. in the absence of bromine.[289] The mechanism of the decomposition is probably

$$\begin{aligned} Br_2 + h\nu &\rightarrow 2Br \\ Br + ClO_2 &\rightarrow BrO + ClO \\ BrO + ClO_2 &\rightarrow Br + ClO_3 \end{aligned}$$

Formation of ClO_3 radicals appears a necessary postulate in order to account for the oxide Cl_2O_6 as the main product of the reaction.[348] The decomposition of chlorine monoxide into chlorine and oxygen is also sensitized by bromine for light of wave-length 5460 A.; in this and in the sensitized decompositions of bromochloroparaffins, the primary step is the dissociation of the bromine molecule into atoms.[348]

The reactions of bromine with fluorine (leading to the formation of a monofluoride, trifluoride, or pentafluoride according to the conditions employed) and with chlorine (leading to the formation of the unstable monochloride) are described on page 147 and page 476 respectively. The reaction with iodine is discussed in detail in Section XXV. Sulphur and bromine, when heated in a sealed tube, yield only the bromide S_2Br_2; selenium and bromine vapours combine to form a dibromide $SeBr_2$, stable between 250° and 500°, which on cooling disproportionates to give bromine and the bromides Se_2Br_2 and $SeBr_4$.[290] Tellurium and bromine react at room temperature, forming tellurium tetrabromide;[291] it seems doubtful therefore whether the suggested use of a tellurium strip as a detector for atomic bromine[339] is very satisfactory. The rate of the well-known oxidation of sulphur in aqueous suspension by bromine appears to be somewhat affected by the salt concentration when the oxidation is carried out in solutions containing sodium chloride or concentrations of lithium chloride higher than 4 N.; this matter has not, however, been investigated in any detail.[292] It has been established that sparking radon and bromine, or exposing them to ultra-violet light, effects no combination.[293]

Sodium in the massive state is without action on bromine (Mellor, II, 92); this system is obviously thermodynamically unstable, however, and under the influence of mechanical shock, detonation occurs.[294] Under the conditions of the sodium flame reaction, bromine reacts more rapidly than methyl iodide.[295] The primary reaction between sodium and bromine as vapours is

$$Na + Br_2 \rightarrow NaBr + Br + 40 \text{ kg.-cal.}$$

This is accompanied by luminescence Secondary reactions are

$$Na + Br \rightarrow NaBr + 86 \text{ kg.-cal.}$$

Refs. p. 718

on the walls, without luminescence, and

$$Na_2 + Br \rightarrow NaBr + Na + 68 \text{ kg.-cal.}$$

in the gas phase, with luminescence.[296] The energy-distribution for electrons emitted in the reaction between bromine and the sodium-potassium alloy NaK_2 has been investigated.[297]

Silver is slowly attacked by bromine; presence of water does not affect the rate of attack, but presence of bromide ions accelerates it.[298] These observations are doubtless to be explained by the insolubility of silver bromide in water and its solubility in solutions of bromides owing to the formation of a complex ion such as $AgBr_2^-$. Zinc and bromine at room temperature do not react to any considerable extent in the absence of a solvent or in the presence of benzene, carbon tetrachloride or petroleum ether.[299,300] In the presence of water or ethyl ether, however, reaction occurs; ether dissolves zinc bromide to form a compound $ZnBr_2,(C_2H_5)_2O$.[300] Aluminium foil, if gently warmed, reacts with bromine with incandescence and the formation of aluminium bromide;[301] the volatility of the bromide prevents the formation of a protective coating.

For the reaction of tin with bromine in carbon tetrachloride, chloroform or ethylene dibromide, the reaction is of the first order with respect to the bromine concentration, and the velocity constant is proportional to the fluidity of the solvent and to the absolute temperature. The dependence of the velocity constant at 20° on the rate of stirring is expressed by the equation

$$k = Bs + k_0$$

where B is a constant, s is the rate of rotation of the cylinder of tin used, and k_0 is the velocity constant when there is no stirring. These results agree with those expected on the basis of the diffusion theory.[302]

Pure dry bromine attacks iron or mild steel only slightly, a protective layer of bromide being formed; in the presence of water, however, a hydrated bromide, which will not adhere to the surface, is produced.[299] Platinum does not react under ordinary conditions, but if bromine atoms are produced thermally (*e.g.*, at 1200°) or photochemically, attack on the platinum takes place; except at temperatures so high that a bromide volatilizes, however, attack is limited to a surface reaction.[303,304]

Fuming nitric acid and bromine at room temperature form bromic acid and nitrogen oxides.[305] Bromine and nitrogen dioxide form a eutectic containing about 72% of N_2O_4 (m.p. −16·6°), but there is no indication of the formation of nitryl bromide in this system.[306] The compounds also fail to react when kept in sealed tubes in the dark or in ultra-violet light, or when heated at 100°.[306] The reaction

$$2NO_{(g)} + Br_{2(g)} = 2NOBr_{(g)}$$

is remarkable as one of the few examples of a third order reaction;[307,308] catalysis of the nitric oxide–chlorine reaction by bromine is attributed to the intermediate formation of nitrosyl bromide.[309]

In the absence of water, bromine reacts with sodium or silver azide according to the equation

$$MN_3 + Br_2 = MBr + BrN_3,$$

forming the highly unstable bromine azide (m.p. *ca.* −45°). In the presence of water, however, the overall reaction becomes:[310]

$$2MN_3 + Br_2 \rightarrow 2MBr + 3N_2$$

The mechanism of the reaction in aqueous solution is

$$N_3^- + Br_2 \rightleftharpoons N_3Br_2^- \rightleftharpoons N_3Br + Br^-$$

$$N_3Br + N_3^- \rightarrow 3N_2 + Br^-$$

The equilibrium is rapidly established, and the bromine azide-azide ion reaction determines the overall rate. The reaction is strongly catalyzed by thiosulphate or tetrathionate, though these ions are oxidized to sulphate while the reaction proceeds. The ratio (moles of bromine consumed)/(moles of thiosulphate or tetrathionate oxidized) increases up to 110 with increasing dilution of thiosulphate or tetrathionate, suggesting a chain reaction involving the ion $S_2O_3Br^-$.[311]

The kinetics of the dark reaction between bromine and nitrite ion in aqueous solution between 0° and 40° indicate that the reaction proceeds by two independent mechanisms, both of the first order with respect to the concentration of bromine, but of orders one and two with respect to the nitrite ion concentration.[312] The suggested mechanisms are

$$Br_2 + NO_2^- \rightleftharpoons Br_2NO_2^- \quad \text{(fast)}$$

then either

$$Br_2NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2Br^- \quad \text{(slow)}$$

or

$$Br_2NO_2^- + NO_2^- \rightleftharpoons (NO_2)_2Br^- + Br^- \quad \text{(fast)}$$

$$(NO_2)_2Br^- + H_2O \rightarrow HNO_2 + H^+ + NO_3^- + Br^- \quad \text{(slow)}$$

The environmental effects of potassium bromide, sodium bromide, potassium nitrate, and sodium nitrate are similar to their effects in the much better-known nitrite-iodine reaction.[312] The photochemical reaction between the same substances at 0° and 10° has also been studied, using light of wave-lengths 4360 A. and 3650 A.[313] The quantum yield, measured as (bromine + tribromide ion) disappearing per absorbed quantum, is about 0·2 and is nearly independent of experimental conditions. In the photochemical reaction the overall rate is entirely determined by the rate of production of bromine atoms by the reaction

$$Br_3^- + h\nu \rightarrow 2Br + Br^-$$

or

$$Br_3^- + h\nu \rightarrow Br + Br_2^-$$

Bromine reacts at room temperature with barium oxide, strontium oxide, argentous oxide, bismuth trioxide, cuprous oxide, chromic oxide, vanadium dioxide and ceric oxide, giving bromides, oxybromides or bromates.[314] The reaction with mercuric oxide is described in detail on page 747. Oxides of aluminium, iron, zinc, nickel, cupric copper, titanium, selenium, molybdenum and tungsten are not attacked. Metal sulphides and bromine usually react to give disulphur dibromide and metal bromides.[314]

Qualitative observations on the bromine-potassium bisulphite reaction in aqueous solution show that the speed of the reaction is markedly dependent on the hydrogen-ion concentration, being a minimum near the neutral point.[315] Sulphur monoxide reacts rapidly with bromine, forming thionyl bromide.[316] Bromine and nickel carbonyl react according to the equation[317]

$$Ni(CO)_4 + Br_2 \rightarrow NiBr_2 + 4CO.$$

The reaction between the liquids proceeds with explosive violence, but their vapours diluted with nitrogen or their solutions in carbon tetrachloride react quietly.

Bromine vapour at 550–600° reacts with stannous oxide or fluoride:[318]

$$2SnO + 2Br_2 \rightarrow SnO_2 + SnBr_4$$

$$2SnF_2 + 2Br_2 \rightarrow SnF_4 + SnBr_4$$

Bromine reacts with aqueous solutions of chlorites mainly according to the equation

$$2ClO_2^- + Br_2 \rightarrow 2Br^- + 2ClO_2$$

Rather less than the theoretical amount of bromine is consumed in the decomposition of the chlorite, however; bromine appears to catalyze the autodecomposition of the chlorite ion into chlorate and chloride.[319]

Bromine is reduced to bromide by hydrogen peroxide and bromide is simultaneously oxidized to bromine in the same solution; the former reaction also involves the liberation of oxygen. The mechanisms of these reactions have been investigated in detail,[321-325] and the results have been summarized by Yost and Russell.[332] According to Bray and Livingston, the principal reactions are:

$$H_2O_2 + 2H^+ + 2Br^- \rightarrow Br_2 + 2H_2O$$

and

$$H_2O_2 + Br_2 \rightarrow O_2 + 2H^+ + 2Br^-$$

When the rates of these reactions are equal, a steady state, in which the net result is the catalytic decomposition of hydrogen peroxide, is reached. Under these conditions the kinetic equation is reported to be

$$-\frac{d}{dt}[H_2O_2] = k[H_2O][H^+][Br^-]$$

Before the steady state is attained, the rates of formation and disappearance of bromine are given by

$$\frac{d}{dt}[Br_2] = k_1[H_2O_2][H^+][Br^-]$$

and

$$-\frac{d}{dt}[Br_2] = k_2\frac{[H_2O_2][Br_2]}{[H^+][Br^-]}$$

These observations have been interpreted as suggesting the mechanism;

$$\begin{array}{lll} H_2O_2 + H^+ + Br^- & \rightarrow HOBr + H_2O & \text{(slow)} \\ H_2O_2 + HOBr & \rightarrow H^+ + Br^- + H_2O + O_2 & \text{(slow)} \\ H_2O + Br_2 & \rightarrow H^+ + Br^- + HOBr & \text{(fast)} \end{array}$$

Unfortunately an independent examination of the reaction by Griffith and McKeown has led to the conclusion that the steady state in this reaction is non-existent;[327] the position is therefore at present obscure.

The photochemical reaction between bromine and hydrogen peroxide in aqueous solution is a chain reaction of quantum yield varying between 2 and 130 according to the experimental conditions.[326-328] The rate is determined, as in the photo-oxidation of nitrite by bromine, by the rate of formation of bromine atoms. The mechanism proposed is:[328]

$$\begin{array}{lll} & Br_2 + h\nu \rightarrow 2Br & \\ \text{or} & Br_3^- + h\nu \rightarrow Br_2^- + Br & \text{(rate-determining)} \\ & Br^- + Br \rightleftharpoons Br_2^- & \text{(fast)} \end{array}$$

$$\left.\begin{array}{l} Br + H_2O_2 \rightarrow HO_2 + H^+ + Br^- \\ HO_2 + Br_2 \rightarrow O_2 + H^+ + Br^- + Br \end{array}\right\} \text{(chain-propagating)}$$

$$\left.\begin{array}{l} Br + Br_2^- \rightarrow Br_3^- \\ Br_2^- + Br_2^- \rightarrow Br_3^- + Br^- \\ Br + Br \rightarrow Br_2 \end{array}\right\} \text{(chain-terminating)}$$

The reaction between bromine and a phosphite appears to be composite, oxidation of the $H_2PO_3^-$ and HPO_3^{--} ions proceeding independently with different, but not widely different, rates:[329]

$$Br_2 + H_2PO_3^- + H_2O \rightarrow H_2PO_4^- + 2HBr$$

$$Br_2 + HPO_3^{--} + H_2O \rightarrow HPO_4^{--} + 2HBr$$

In this instance the oxidizing agent appears to be molecular bromine and not the Br_3^- or BrO^- ions.[329] The oxidation of hypophosphite by bromine is more complex;[330] the salient features of this and the analogous oxidation by iodine are summarized by Yost and Russell.[332] The first oxidation product is phosphite, and further oxidation of this is sufficiently slow to be neglected in investigating the reaction whose stoicheiometry is represented by

$$H_3PO_2 + Br_2 + H_2O = H_3PO_3 + 2H^+ + 2Br^-$$

Explanation of the results appears to require the simultaneous oxidation of the hypophosphite ion and of a tautomeric or hydrated form of hypophosphorous acid (written here, following Yost and Russell,[332] as H_5PO_3). The mechanism of the oxidation is then suggested to be:

$$\begin{array}{lcll} H_2PO_2^- + Br_2 + H_2O & \rightarrow & H_3PO_3 + H^+ + 2Br^- & \text{(slow)} \\ H_2PO_2^- + H^+ & \rightleftharpoons & H_3PO_2 & \text{(fast)} \\ H_3PO_2 + H_3O^+ & \rightleftharpoons & H_5PO_3 + H^+ & \text{(slow)} \\ H_5PO_3 + Br_2 & \rightarrow & H_3PO_3 + 2H^+ + 2Br^- + H_2O & \text{(slow)} \end{array}$$

Reinvestigation of this reaction appears desirable.

The oxidation of hypophosphates to phosphates by bromine is quantitative at pH 8, at which hydrogen ion concentration the rate is a maximum.[331] Cupric ions are catalysts for the reaction only in more alkaline solutions.[331] The kinetics of this reaction, however, have not been investigated in any detail.

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SECTION XXIII

THE PREPARATION OF HYDROGEN BROMIDE AND HYDROBROMIC ACID

By A. A. WOOLF

The kinetics of the thermal and photochemical reactions between hydrogen and bromine have been described on page 706. On an industrial scale, hydrogen bromide and hydrobromic acid are almost invariably obtained from hydrogen and bromine: the gases combine in the presence of a carbon catalyst at temperatures between 150° and 600° (widely different temperatures appear to have been used successfully).[1-5] Ferric oxide has been used for activation of the catalyst.[2] In one process,[5] hydrogen is passed through liquid bromine at 37–42°, and the resulting mixture of gases is burned on a carbon or porcelain surface the temperature of which is maintained by the heat liberated; the resulting gases are partially cooled, passed over active charcoal at 150-200°, and absorbed in water. Catalysts are not essential so long as the temperature is high enough; the chief difficulty is to avoid, on the one hand explosive combination or, on the other hand, the spontaneous extinction of the hydrogen-bromine flame.

In the catalysis of the reaction by charcoal, the basal planes of the graphite crystal appear to be active:[6-8] at 150°, 100 carbon atoms in the surface will effect the formation of about 20 molecules of hydrogen bromide per hour.[8] Catalysts prepared by heating at 1300° and 3000° are equally effective at 150°.[6] Other catalysts, including copper, chromic oxide, aluminium, iron, magnesium oxide, calcium bromide and platinized asbestos, have also been used.[9,10]

In the laboratory, anhydrous hydrogen bromide may be prepared by bubbling hydrogen through bromine at 38°, and passing the vapours through a combustion tube maintained at a dull red heat.[11] In another essentially similar method, platinized silica gel at 375° is used as a catalyst.[10] The former method has been applied to the preparation of deuterium bromide from deuterium and bromine.[12] For the preparation of anhydrous hydrogen bromide from a bromide, phosphoric acids are valuable reagents;[25-27] in one method, syrupy phosphoric acid is added to a mixture of sodium bromide and phosphorus pentoxide, and the gas is dried with calcium bromide.[25]

Other convenient laboratory methods of preparation make use of the interaction of bromine and hydrocarbons: naphthalene,[13] petroleum (in the presence of aluminium bromide as a catalyst),[14] or tetrahydronaphthalene[15,16] may be used. Tetrahydronaphthalene (dried by passing dry air through the liquid for 30 mins.) and bromine react steadily at room temperature; any bromine present in the hydrogen bromide is removed by passing the gas through more tetrahydronaphthalene.[15] Such methods necessarily involve the loss of half of the bromine taken, owing to bromination of the hydrocarbon; the yields, however, are as high as 94% of the calculated value.

Aqueous solutions of hydrogen bromide may be made either directly from the gas or by interaction of bromine with water or steam in the presence of charcoal.[17-19] Hydrogenation of bromine water with a platinum catalyst yields hydrobromic acid quantitatively.[20] A strong solution of hydrobromic acid, substantially free from bromine, is said to be formed by heating a concentrated solution of sodium bromide with concentrated sulphuric acid.[21] Constant boiling point hydrobromic acid is prepared from potassium bromide (120 g.), water (200 ml.) and concentrated sulphuric acid (90 ml.). During the addition of the acid, the temperature should remain below 75° to avoid liberation of bromine; after cooling to room temperature and filtering off potassium bisulphate, the solution is distilled, the fraction boiling at 125 ± 1° under 760 mm. pressure being collected.[22,23] In an alternative procedure, a little stannous chloride is added to the mixture of potassium bromide and dilute sulphuric acid; after allowing it to stand overnight, the solution is decanted from the bisulphate and distilled.[24]

Hydrogen bromide or hydrobromic acid may be obtained by combining bromine and sulphur and hydrolyzing the product with water or superheated steam.[28-31] The stoicheiometry of this process is expressed by the equation:

$$3Br_2 + S + 4H_2O \;=\; 6HBr + H_2SO_4$$

Nearly anhydrous hydrogen bromide may also be obtained by a modification of Scott's classical procedure (Mellor, II, 168): interaction of bromine and water in excess of liquid sulphur dioxide.[32] The decomposition of cadmium bromide by hydrogen sulphide at 500° has also been investigated; at this temperature the yield is 89%:[33]

$$CdBr_2 + H_2S \rightleftharpoons CdS + 2HBr.$$

Deuterium bromide has been made from heavy water and phosphorus tribromide.[35]

Hydrogen bromide is best purified by fractional distillation or condensation.[35,36] It cannot be dried with concentrated sulphuric acid, and the use of phosphorus pentoxide appears undesirable owing to the formation of traces of bromine and phosphorus oxybromide.[26,33,34] The best drying agents are aluminium oxide (prepared by gentle ignition of the hydroxide[37]) and the well-established calcium bromide. Bromine present in hydrogen bromide is usually removed by combination with red phosphorus (Mellor, II, 168), but mercury may also be used.[36]

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SECTION XXIV

THE PHYSICAL AND CHEMICAL PROPERTIES OF HYDROGEN BROMIDE

By A. A. WOOLF

STRUCTURE

Solid hydrogen bromide is trimorphous, with transition points at 89·75, 113·62 and 116·86°K.[1] The first of these corresponds to the 93·50°K. transition point for deuterium bromide; the two others replace the 120·26° transition point in deuterium bromide.[1] The theoretical aspects of this disappearance of a phase on isotopic substitution have been discussed.[1] These results agree with earlier observations[22] on the heat capacity of solid hydrogen bromide.

The structures of two forms of hydrogen bromide have been established by *X*-ray analysis.[2] The face-centered cubic form, with $a = 5{\cdot}76 - 5{\cdot}78$ A., 4 mols. per unit cell, and a calculated density of 2·76 - 2·80, is stable only over a very narrow range of temperature (probably between the two higher transition points for hydrogen bromide). This fact may account for the failure of other workers[3] to detect its existence. The stable form below 100°K. has a face-centered rhombic structure, with $a = 5{\cdot}55$, $b = 5{\cdot}64$, $c = 6{\cdot}06$ A., 4 mols. per unit cell, and a calculated density of 2·81;[2] the space group is V^7 or V_h^{23}. This structure is nearly isomorphous with that of solid hydrogen iodide, the axial ratios being $a{:}b{:}c$ 0·985:1:1·075 compared with $c{:}a = 1{\cdot}075$ for the tetragonal unit cell of the latter compound. The experimentally determined density at -195° is 2·90; the molecular volume is 0°K. is estimated to be 27·3 c.c.[4]

Analysis of the pure-rotational and rotational-vibrational spectra (see also page 789) leads to values of[5] 1·420 and[6] 1·414 A. respectively for the internuclear distance. The force constant of the H-Br bond is $4{\cdot}06 \times 10^{-5}$ dynes cm.$^{-1}$,[6] or, corrected for anharmonicity,[7] $3{\cdot}8 \times 10^{-5}$ dynes cm.$^{-1}$ In the series of hydrogen halides the force constants obey the relationship fr^2 = constant, where r is the internuclear distance.[7]

Although hydrogen bromide is a relatively simple molecule, a precise description of the bond between the atoms is difficult. An early discussion, based on crystallographic and viscosity data, on atomic size led to the conclusion that an ionic structure, H^+Br^-, would require the radius of the H^+ ion to be 0·26 A.;[8] this discussion appears to assume, however, that the radius of the bromide ion is nearly the same as that of the bromine atom - an assumption now known to be far from true (see page 695). The fact that the ionization potential of hydrogen (311 kg.-cal.) is so much greater than the electron affinity of bromine (80·5 kg.-cal.) appears to be a conclusive arguement against the ionic structure for isolated molecules in the vapour phase.

Another approach, essentially that of Pauling,[9,10] is to regard the linkage as a single covalent bond with partial ionic character. The observed bond energy in hydrogen bromide (derived from the convergence limit of the ultraviolet spectrum) is 87·3 kg.-cal. mole^{-1}; the mean value of the H-H in H_2 and Br-Br in Br_2 bond energies is only 74·7 kg.-cal.mole^{-1}. These data are interpreted by Pauling[9,10] as indicating that the H-Br bond has about 11% ionic character. This estimate appears to agree well with that made from the observed dipole moment of 0·80 Debye units;[11] a structure H^+Br^- would have a moment $r \times e$, where r = internuclear distance and e = charge on the electron, *i.e.*, about 6·7 Debye units. Theoretical and mathematical discussions have been given of the semi-empirical calculation of the bond moment from the energies of idealized covalent and ionic bonds;[12] the effect of ionic-covalent and single-double bond resonance on the force constant in the vapour phase and in non-ionizing solvents;[13] and the relation of potential energy to the polarizability, the electron affinity of bromine, and the internuclear distance.[14]

SURFACE TENSION, DENSITY AND VISCOSITY

A redetermination of the density and surface tension of liquid hydrogen bromide (by the capillary rise method)[15] gave the values recorded in Table I.

TABLE I. - DENSITY AND SURFACE TENSION OF LIQUID HYDROGEN BROMIDE

t°C.	−67·1	−60·0	−46·0
γ (dynes cm.$^{-1}$)	27·07	22·54	22·67
d (g. c.c.$^{-1}$)	2·717	2·238	2·174

From these data the parachor was evaluated as 81·5. The coefficient of thermal expansion is 0·002119, the temperature coefficient of surface tension is 0·2085 dyne cm.$^{-1}$ deg.$^{-1}$, and the Ramsay-Shields constant is 1·91; the last quantity indicates that the liquid is no more than slightly associated.[15] The surface tension of solutions of hydrobromic acid decreases with increasing concentration,[16] but detailed results have not been given.

The viscosity of gaseous hydrogen bromide is 1·835 ± 0·0027 × 10^{-4} c.g.s. units at 18·7° and 2·365 ± 0·0019 × 10^{-4} c.g.s. units at 100·2°.[17] Sutherland's constant for the gas is 375.[17] The viscosity (relative to $\eta_{H_2O} = 1$) at 25° of aqueous solutions is given in Table II.

TABLE II. - VISCOSITY OF AQUEOUS SOLUTIONS OF HYDROGEN BROMIDE

Concentration,[19] M.	0·01	0·02	0·05	0·1	0·5	1
η	1·0003	1·0007	1·0016	1·0033	1·0165	1·0327
Concentration,[18] M.	1·009	1·997	4·021	5·994	8·759	
η	1·035	1·072	1·172	1·324	1·613	

THERMAL PROPERTIES

The vapour pressures of liquid and gaseous hydrogen bromide and deuterium bromide are given by the equations:[20]

$$\log p\ (\text{HBr liq.}) = 7{\cdot}465 - 945{\cdot}7\ T^{-1}$$
$$\log p\ (\text{HBr solid}) = 8{\cdot}309 - 1103\ T^{-1}$$
$$\log p\ (\text{DBr liq.}) = 7{\cdot}517 - 956{\cdot}5\ T^{-1}$$
$$\log p\ (\text{DBr solid}) = 8{\cdot}306 - 1103\ T^{-1}$$

Slightly different values have been given for the vapour pressure of hydrogen bromide by other authors,[21] who proposed the equations:

$$\log p\ (\text{HBr solid}) = 7{\cdot}503 - 2202\ T^{-1{\cdot}1602}$$
$$\log p\ (\text{HBr liq.}) = 7{\cdot}503 - 1037{\cdot}2\ T^{-1{\cdot}0160}$$

The b.p. of deuterium bromide is identical with that of hydrogen bromide;[20] the latter quantity is given as 206·3°K.,[20] 206·0°K.,[21] or 206·38°K.[22] The m.p. of hydrogen bromide is 186·24°K.;[22] that of deuterium bromide is 185·62° K.[23] The triple points are: HBr, 186·24°K.[22] or 186·2°K.;[20] DBr, 185·7°K.[20]

The triple point pressure of deuterium bromide is 232 mm.[28]

The latent heat of fusion of hydrogen bromide, determined calorimetrically, is variously given as 620[23] and 575·1[22] g.-cal. mole^{-1}; the latter value was used in the evaluation of the entropy (which agrees very well with the spectroscopic value) and appears therefore to be the more reliable. The value for deuterium bromide is 574·2 g.-cal. mole^{-1}.[28] The latent heat of vaporization has been determined as 4210 ± 4 g.-cal.mole^{-1} (calorimetrically)[22] and 4405 g.-cal.mole^{-1} (from the vapour pressure curve);[21] the former value is preferred. The best values for the entropies of vaporization of hydrogen and deuterium bromides are 20·40 and 20·63 g.-cal.deg.$^{-1}$ mole^{-1} respectively.[20]

The critical temperatures of hydrogen and deuterium bromides are[24,25] 89·8° and[25] 88·8°. The critical pressure of hydrogen bromide is 84 atm.;[24] this value is discussed in a review of critical constants of hydrogen compounds isoelectronic with the inert gases.[26] The internal pressure at the boiling point, calculated from the b.p., molecular volume, and critical constants, is 2277 atm.[27] The thermal conductivity of solid hydrogen bromide, measured in the temperature range 78 – 142 °K., shows a rapid increase at the 89·75 °K. transition point.[50] The imperfection of hydrogen bromide vapour has been considered in a theoretical review by Curtiss and Hirschfelder;[51] experimental results are given in Mellor, II, 175.

The specific heat of hydrogen bromide has been investigated by Giauque and Wiebe[22] and by Eucken and Karwat;[23] their results differ considerably, those of the latter authors being rather higher at all temperatures. Since the entropy determined from the results of Giauque and Wiebe agrees with that determined spectroscopically, their results are preferred; a selection is given in Table III.

TABLE III. - VALUES OF C_p FOR HYDROGEN BROMIDE

T (°K.)	C_p (g.-cal. mole^{-1})	T (°K.)	C_p
15·72	1·831	113·31	135
30·16	3·955	113·37	1 90
57·80	6·171	114·13	19·32
80·03	9·368	115·76	13·06
89·23	29·08	116·76	239
89·39	114	116·86	860
89·49	268	118·99	10·79
89·50	483	172·86	11·91
89·59	187	186·24	m.p.
90·01	17·02	189·93	14·20
90·91	9·87	205·11	14·31
111·47	12·58	206·38	b.p.

The nature of the transitions associated with the abrupt variations in specific heat is not yet firmly established. From the heat changes associated with phase transitions and these results, the entropy at the b.p. was evaluated as 44·9 ± 0·1 g.-cal. deg.$^{-1}$ mole^{-1}; the values calculated from spectroscopic data are 47·53 and 44·92 g.-cal. deg.$^{-1}$ mole^{-1} at 25° C. and the b.p. respectively.[22]

The heat capacity of hydrogen bromide up to 2000 °K., calculated from spectroscopic data, is given to within about 3% by the empirical equation[52]

$$C_p = 6{\cdot}30 + 0{\cdot}001819\,T - 0{\cdot}000{,}000{,}345\,T^2.$$

The heat capacities of deuterium bromide and deuterium bromide-hydrogen bromide mixtures have also been investigated.[1,28] The heat capacity of deuterium bromide at any given temperature is a little greater than the corresponding value for hydrogen bromide;[28] representative values are given in Table IV.

TABLE IV.- VALUES OF C_p FOR DEUTERIUM BROMIDE

T (°K.)	C_p
29·3	3·92
56·9	6·44
91·0	18·36
93·7	74·15
95·3	10·79
117·5	14·55
119·6	43·62
122·9	11·63
160·7	12·34
183·7	13·49
185·6	m.p.
190·5	14·95
205·8	15·05

The calorimetrically determined entropy at the b.p. (206·38 °K.) is 46·31± 0·15 g.-cal. deg.$^{-1}$ mole^{-1}; that calculated statistically is 46·29 g.-cal. deg.$^{-1}$ mole^{-1}.[28]

The chemical constant for hydrogen bromide was evaluated from vapour pressure and calorimetric data as[29] 0·53 ± 0·07 or 0·59;[30] these values are derived from vapour pressures expressed in atmospheres. The zero-point energy and heat of sublimation of hydrogen bromide at 0°K. have been calculated, using the experimental data of other workers[22] as 207 and 5428 g.-cal. mole^{-1} respectively.[21]

The value of + 8·6 kg.-cal. mole^{-1} for the heat of formation of gaseous hydrogen bromide from liquid bromine and hydrogen (Mellor, II, 177) remains very near the best value: the Bureau of Standards selected data for hydrogen bromide are[32]

$$\Delta H^\circ = -8{\cdot}66 \text{ kg.-cal. mole}^{-1}$$
$$\Delta G^\circ = -12{\cdot}72 \text{ kg.-cal. mole}^{-1}$$
$$S^\circ = 47{\cdot}437 \text{ g.-cal. deg.}^{-1} \text{ mole}^{-1}$$

Their value for the heat of formation of hydrobromic acid at infinite dilution is + 28·90 kg.-cal. mole^{-1}. Somewhat lower values for the heats of formation of the gas (+ 7·84 kg.-cal. mole^{-1}) and the acid at infinite dilution (+ 27·85 kg.-cal. mole^{-1}) have been reported by Roth,[33] who also reports that the heat of solution does not decrease with increasing dilution. Heats of solution in organic solvents, derived from solubility measurements, have been reported (see page 734). Partial molal heat capacities in aqueous hydrobromic acid have been discussed.[67,70]

OPTICAL, MAGNETIC AND ELECTRICAL PROPERTIES

The molecular refraction of hydrogen bromide, derived from measurements of refractive index (Mellor, II, 178) is[34] 9·14 or[35] 8·48. In aqueous solution at the following dilutions, the molecular rotation is:[37]

% by wt. HBr	4·304	9·422	23·032	48·92
$R_{\text{mol.}}$	12·18	12·127	12·075	11·81

The change in optical properties on solution in water results from complete ionization.[37,38] Attempts have been made to correlate light scattering by gases (including hydrogen bromide) in the visible region with molecular structure.[39]

The dielectric constant of hydrogen bromide obeys the Debye relationship over the temperature range 217–599 °K.; the dipole moment, calculated from the following values,[41] is 0·80 Debye units.[40]

T	217·5°	294·4°	338·9°	599·1°
ϵ at 760 mm.	1·00454	1·002796	1·002228	1·000943

The dipole moment is increased on solution, as is illustrated by the following values.

Solvent	CCl_4		n-C_7H_{16}	C_6H_6		1:4-dioxan
t	20°	30°	30°	20°	30°	30°
μ in D.	0·96[43]	0·93[42]	1·02[42]	1·01[43]	1·08[42]	2·85[42]

The high value in dioxan would appear to suggest partial oxonium-salt formation.

The dielectric constants of hydrogen bromide and a number of other gases obey the empirical relationship

$$\epsilon = 1 + 3\sqrt{3\pi}.N_0.r^3$$

where N_0 is the Avogadro number and r the internuclear distance.[44,45] The complex dielectric properties of solid hydrogen bromide have been studied. The dielectric constant varies with frequency and two dispersions are observed. Only the first disappears abruptly at the 90 °K. transition point. The activation energy of the dielectric process can be obtained from the temperature variation of the critical frequency -- the frequency of the maximum dielectric constant - for deuterium bromide but not for hydrogen bromide.[55-58] The ionization potential determined by the electron impact method is apparently for the process

$$HBr \rightarrow H^+ + Br^-.$$

The value of 13·3 e.V.[47] is derived by correction of the original result.[46] There is no direct correlation between breakdown potential and ionization potential of gases, including hydrogen bromide. The former potential, however, is a function of other physical properties such as internuclear distance and critical temperature. The correlation of breakdown potential and other physical quantities has been discussed[53,54] for hydrogen bromide and several other gases.

The diamagnetic susceptibility of hydrogen bromide does not appear to have been determined; in aqueous solution the value is[59] $-33{\cdot}0$ or $-32{\cdot}5 \times 10^{-6}$ c.g.s. units.[48] The magneto-optical molecular rotation is interpreted as demonstrating the existence of undissociated molecules in concentrated aqueous solution.[49]

AQUEOUS SOLUTIONS OF HYDROGEN BROMIDE

The composition of constant boiling point hydrobromic acid has been the subject of several investigations, with the following results for the percentage by weight of hydrogen bromide and the b.p.: 47·5%, 126°;[60] 47·8 ± 0·03%, 125°;[61] 47·63%, 124·3°.[62] The last set of values appears the most precise. All these values refer to a pressure of 760 mm. At this pressure, the values given in Table V are typical for the boiling-points and % HBr by weight in aqueous solutions.[60]

TABLE V.- BOILING POINTS AT 760 mm. OF AQUEOUS SOLUTIONS OF HYDROGEN BROMIDE

B.p. °C.	22	28	40	110	124·5	126	123·6	116·5	107·5	103·5	101·25
% HBr	60	56·7	53·6	50·8	48·4	47·5	43·8	38·2	24·8	15	6·6

The temperature of distillation, *t*, and % HBr by weight in the distillate are given in Table VI:[60]

TABLE VI.- DISTILLATION TEMPERATURES AND DISTILLATE COMPOSITIONS FOR AQUEOUS HYDROGEN BROMIDE

t	25°	45°	90°	124°	126°
% HBr	99	97	95	57·5	47·5
t	123°	116°	106·5°	102°	100·5°
% HBr	24·5	10·5	0·74	0·1	0·03

The effect of pressure on the b.p. and composition of constant boiling hydrobromic acid[62] is shown in Table VII.

TABLE VII.- EFFECT OF PRESSURE ON THE B.P. OF CONSTANT-BOILING HYDROBROMIC ACID

p (mm.)	100	200	400	600	800	1000	1200
b.p. °C.	74·12	90·35	107·00	117·82	125·79	132·12	137·34
% HBr	49·80	49·28	48·47	47·95	47·56	47·27	47·03

The pressure of hydrogen bromide over 6N-hydrobromic acid is 0·00077 mm. at 15°, 0·0015 mm. at 25° and 0·0028 mm. at 35°.[63] Table VIII gives some values for the composition of hydrobromic acid and of the vapour above it:[64]

TABLE VIII.- COMPOSITION OF HYDROBROMIC ACID AND ITS VAPOUR AT SELECTED TEMPERATURES

At 19·93°,					
Mole % HBr in liquid	16·94	19·6	21·38	22·73	
Mole % HBr in vapour	2·53	18·32	55·62	80·00	
Partial pressure of HBr (mm.)	0·1	0·8	2·8	6·5	
Partial pressure of H_2O (mm.)	5·0	3·5	2·2	1·6	
At 54·8°,					
Mole % HBr in liquid	16·94	18·20	19·20	21·12	25·17
Mole % HBr in vapour	0·05	13·15	25·16	54·90	96·30
At 79·9°,					
Mole % HBr in liquid	16·52	19·40	24·33		
Mole % HBr in vapour	6·60	33·3	90·75		

The Duhem–Margulès equation is obeyed by solutions containing up to 55% by weight of hydrogen bromide.[65] The importance of a high degree of ionic dissociation for the formation of an azeotrope of boiling-point higher than those of the components has been discussed by Simmons in a review of azeotrope formation.[66]

The unspecified temperature for densities of hydrobromic acid given previously (Mellor, II, 186) appears to be 20°; it should, however, be pointed out that the sources and values are not always in complete agreement with those chosen by the compilers of the International Critical Tables. Isolated data have also been recorded in the course of other investigations.[18,67,59,36]

Diffusion studies in hydrobromic acid appear to indicate that each 'molecule' carries with it 5·9 molecules of water; in view of the very high mobility of the hydrogen ion, this conclusion seems unreasonable.[68] The term 'solvation number' and its value for the bromide ion are further discussed on page 700. The interaction of water and hydrogen bromide in liquid sulphur dioxide has been investigated by Bagster and Cooling.[69] In the absence of moisture, hydrogen bromide in sulphur dioxide does not conduct electricity; the solution does, however, dissolve one mole of water for each mole of hydrogen bromide, and then becomes a good conductor. On electrolysis, hydrogen and water are liberated at the cathode, bromine at the anode. These results show that the reaction taking place is

$$HBr + H_2O \rightarrow H_3O^+ + Br^-.$$

The HBr–H_2O system (Mellor, II, 184) does not appear to have been further investigated.

The equivalent conductivity at infinite dilution of hydrobromic acid has been reported as[18] 433·7 and[19] 426·2 ohm^{-1} at 25°, and the ionic mobility of the bromide ion as[71] 77·85, 78·1[72] and[73] 78·52 ohm^{-1} at the same temperature. The temperature coefficient of ionic mobility between 18° and 25°, evaluated from these and older results, is[74] 0·0238. In N-hydrobromic acid, the Hittorf transport number of the bromide ion is[75] 0·164; at infinite dilution it is[75] 0·177. Hydrogen overvoltage at different electrodes in several acids (including hydrobromic) has been studied by Russian workers.[76-79]

The activity coefficients of hydrobromic acid have been calculated from the e.m.f. of cells of the type

$$H_2 \;\Big|\; HBr\ (x\ M) \;\Big|\; AgBr \;\Big|\; Ag$$

at 25°:[80]

x	0·0850	0·1086	0·1878	0·2400
e.m.f. (v.)	0·2101	0·1982	0·1812	0·1585
γ	0·824	0·812	0·796	0·795

x	0·3075	0·497	0·755	1·010	1·505
e.m.f. (v.)	0·1463	0·1214	0·0980	0·0804	0·0534
γ	0·787	0·791	0·822	0·864	0·980

Activity coefficients have also been determined, using similar cells, in the presence of sulphate, chloride and added bromide ions.[80-84] By the same method, other authors[67] have since obtained slightly different results for the activity coefficient of hydrobromic acid in the concentration range 0·001-1 M. at temperatures between 0° and 60°. Some of their results are given in Table IX.

TABLE IX. - ACTIVITY COEFFICIENTS OF HYDROGEN BROMIDE IN AQUEOUS SOLUTION

Concentration	0°	15°	25°	45°	60°
0·001 M.	0·967	0·966	0·966	0·964	0·963
0·01 M.	0·910	0·908	0·906	0·904	0·898
0·1 M.	0·812	0·808	0·805	0·797	0·788
1 M.	0·900	0·888	0·871	0·844	0·823

The standard potential of the cell at temperature t°C. is given by the equation[67]

$$E_0 = 0{\cdot}06846 - 0{\cdot}0005185\,(t-30) - 2{\cdot}973 \times 10^{-6}\,(t-30)^2.$$

The thermodynamic properties of solutions containing hydrobromic acid and hydrochloric acid,[81] lithium bromide,[84] sodium bromide[82,83] and potassium bromide[82,83] have also been investigated.

NON-AQUEOUS SOLUTIONS OF HYDROGEN BROMIDE

The Henry's Law constants × 10^{-3} (mm. HBr/mole HBr per 1000 g. of solution) for the solubilities of hydrogen bromide in certain *n*-paraffins[85] are given in Table X.

TABLE X. - HENRY'S LAW CONSTANTS FOR HYDROGEN BROMIDE IN *n*-PARAFFINS

Solvent	25°	35°	45°
n-Hexane	1·64 ± 0·02	1·97 ± 0·08	2·20 ± 0·08
n-Octane	2·01 ± 0·05	2·33 ± 0·07	2·65 ± 0·09
n-Decane	2·15 ± 0·07	2·49 ± 0·07	2·75 ± 0·07

From these figures the heats of solution are calculated to be 2620, 2490 and 2340 g.-cal. mole^{-1} in *n*-hexane, *n*-octane and *n*-decane respectively.[85] It is further deduced that at any given temperature the value of the constant approaches a limit as the length of the chain in the *n*-paraffin increases. The effect of chain-branching has not been studied.[85]

Data have also been recorded for the solubility in *n*-butane and in *n*-hexane at lower temperatures: the Henry's Law constant (in lb./sq. inch/mole fraction HBr) are 443 and 326 for *n*-butane at 25° and 5°, and 348 and 265 for *n*-hexane at 20° and 5°.[89] The heats of solution calculated from these results are 2,510 and 3,050 g.-cal. mole^{-1} for *n*-butane and *n*-hexane respectively.[89] There is no evidence for interaction of aluminium bromide and hydrogen bromide in either of these solvents.[89]

For solutions of hydrogen bromide in benzene, the Henry's Law constant is 15·8 ± 0·5 at 30° and 24·4 ± 0·6 at 50° (in atm. HBr/moles HBr per 1000 g. of solution); the calculated heat of solution is 4200 g.-cal. mole^{-1}, and the heat of mixing liquid hydrogen bromide and liquid benzene is 175 g.-cal.[87] The system does not obey Raoult's Law.[87]

Solubility measurements in toluene, *o*-nitrotoluene and *m*-nitrotoluene have also been recorded; in all these solvents there are negative deviations from Raoult's Law. The Henry's Law constants (in atm. HBr/ moles HBr per 1000 g. solution) are 0·99 for toluene, 1·32 for *o*-nitrotoluene, and 1·42 for *m*-nitrotoluene at 25°.[86] A value of 1·03 for benzene was also obtained;[86] this does not agree with those given above or the calculated heat of solution for a similar range of pressure and concentration, and further investigation appears desirable.

Solutions of hydrogen bromide in chloroform and carbon tetrachloride show positive deviations from Raoult's Law; the Henry's Law constants × 10^5 (here expressed in normality HBr/mm.HBr) are:[88]

	0°	15°	25°
Carbon tetrachloride	8·26 ± 0·01	5·95 ± 0·02	5·03 ± 0·02
Chloroform	9·92 ± 0·03	7·17 ± 0.03	5·97 ± 0.03

The heats of solution are 3230 g.-cal. mole^{-1} in carbon tetrachloride and 3260 g.-cal. mole^{-1} in chloroform.[88]

Hydrogen bromide is only very slightly soluble in liquid hydrogen fluoride.[90] It is miscible in all proprotions with liquid sulphur dioxide; the properties of the solution are referred to on page 732. The fact that the e.m.f. of cells such as Ag AgBr|liq. SO_2, HBr|H_2,Pt are higher than is expected from thermal data is attributed to solvation of the silver salt,[96] but this is not confirmed.

The conductivity of hydrogen bromide in anhydrous methanol has been measured at 25° with the following results:

V(l.)	10	40	160	640	1280
Λ(ohm^{-1}) ref.[91]	128·5	154·0	177·0	189·2	195·0
ref.[92]	124·6	147·4	166·8	181·5	186·5

The equivalent conductivity at infinite dilution is[91] 212·3 or[92] 206·6 ohm^{-1}, and the degree of dissociation in 0·1 N-solution 0·605[91] or 0·603.[92] Data for 0° have also been obtained: at dilutions of 10·88, 62·12 and 879 litres the equivalent conductivity is 97·3, 121·1 and 142·9 ohm^{-1} respectively.[91] In anhydrous ethanol at 25°, the equivalent conductivity is:[92]

V(l.)	10	40	160	640	1280
Λ(ohm^{-1})	42·2	52·8	63·1	72·8	75·7

The equivalent conductivity at infinite dilution is 88·9 ohm^{-1}, and the apparent degree of dissociation in 0·1 N-solution is 0·474.[92] Conductivities in *n*-propanol,[93] *n*-butanol[94] and methanol or ethanol containing water have also been measured,[92] and the apparent degree of dissociation in such solvents has been related to catalytic activity during esterification.

Recorded values of the density and viscosity of solutions of hydrogen bromide in absolute ethanol at 25° are:[95]

Concentration (mole/l.)	0·05	0·2	0·4	0·6
d	0·7889	0·7997	0·8149	0·8292
η (c.g.s. units)	0·01121	0·01194	0·01281	0·01362

For a 0·1 N-solution containing x mole H_2O per litre the values at 25° are[95]

x	0	0·05	0·1
d	0·7928	0·7931	0·7934
η	0·01151	0·01164	0·01175

In anhydrous acetic acid the ionization of hydrogen bromide is very much reduced, but it remains a stronger acid than hydrogen chloride, the pK values being 6·40 and 8·85 respectively.[97] The relative strengths as acids remain in the order HI>HBr>HCl in water, acetonitrile, methanol, ethanol, *n*-propanol, *n*-butanol, pyridine and aniline.[98] From the general discussion of acids given by Bell,[99] it may be inferred that this is due mainly to the decreasing bond strength in the series HI, HBr, HCl; this factor appears to be more important than the increasing solvation energy of the anion as it becomes smaller.

In nitrobenzene (despite its high dielectric constant) hydrogen bromide is almost a non-conductor, the apparent degree of dissociation probably being about 10^{-4}; the equivalent conductivity at a dilution of 40 litres is only 0·0632 ohm^{-1}.[100] The conductivity is, however, greatly increased by the presence of traces of water; this would seem to be for the same reason as in liquid sulphur dioxide, but it is reported that the addition of hydrogen bromide to a solution of water in nitrobenzene produces little lowering of the freezing-point.[100]

ADSORPTION

Crystals of hydrogen bromide at about −110° adsorb radon.[101]

The adsorption of hydrogen bromide by silica gel from −45° to 60° is in general agreement with the Brunauer and Teller theory. Values[102] are given in Table XI. Adsorption from aqueous solution on mercury[105] and charcoal[106] has also been investigated.

Sorption of hydrogen bromide on nickel has been studied in connexion with the role of oxygen in catalyzing the dehydrobromination of organic compounds. Activated adsorption of hydrogen bromide appears to take place. A nickel surface with chemisorbed oxygen adsorbs 3–5 times as much hydrogen bromide as freshly reduced nickel.[103,104] Other workers, however, have reported that hydrogen bromide reacts with reduced nickel in the presence of oxygen, forming nickel bromide and liberating hydrogen.[155,156]

TABLE XI. - ADSORPTION OF HYDROGEN BROMIDE BY SILICA GEL

$-45{\cdot}6^\circ \pm 0{\cdot}5^\circ$; p(mm.)	56·9	174·2	281·4	544·2	776·2
millimoles/g. sorbent	1·130	2·244	3·502	4·380	5·656
$-25^\circ \pm 0{\cdot}2^\circ$; p(mm.)	62·9	138·5	280·9	561·8	779·7
millimoles/g. sorbent	0·494	1·075	1·688	2·607	3·204
$0^\circ \pm 0{\cdot}3^\circ$; p(mm.)	24·0	208·1	348·1	512·9	785·7
millimoles/g. sorbent	0·128	0·673	0·988	1·279	1·723
$35{\cdot}2^\circ \pm 0{\cdot}1^\circ$; p(mm.)	39·2	174·8	357·5	501·0	785·6
millimoles/g. sorbent	0·059	0·222	0·388	0·505	0·738
$60{\cdot}5^\circ \pm 0{\cdot}2^\circ$; p(mm.)	52·0	120·9	351·1	562·1	763·1
millimoles/g. sorbent	0·048	0·091	0·213	0·314	0·402

CHEMICAL PROPERTIES OF HYDROGEN BROMIDE AND HYDROBROMIC ACID

The thermal dissociation of hydrogen bromide is discussed in Mellor, II, 146. More recently, equilibrium constants for the reaction

$$HBr_{(g)} \rightleftharpoons \tfrac{1}{2}H_2(g) + \tfrac{1}{2}Br_2(g)$$

have been evaluated from spectroscopic data:[109]

T	300	400	600	800	1200	1600	°K.
$\log K$	−9·37	−7·16	−4·93	−3·80	−2·65	−2·07	

The rate of decomposition is not affected by traces of moisture.[123,124]

For the exchange reaction

$$HBr + HD \rightleftharpoons H_2 + DBr$$

the equilibrium constants have been calculated from spectroscopic data, it being assumed that molecular rotations, but not vibrations, are all excited:

$$\ln K = 2{\cdot}414 - 128{\cdot}11/T$$

Experimental determinations between 300° and 650°K. agree with the calculated values within the experimental error.[110]

Hydrogen bromide and pure ozone react instantaneously at room temperature, the mixture exploding except at low pressures (2–3 cm.). The reaction proceeds by a chain mechanism involving hydroxyl radicals formed at the walls. At −104°, where the reaction can be studied conveniently, the net change is expressed approximately by the equation

$$2HBr + O_3 = H_2O + Br_2 + O_2.$$

In the non-explosive reaction the rate is proportional to the first powers of the hydrogen bromide and ozone pressures; the reaction is inhibited by inert gases in the order $He < A < H_2 < O_2$; from the temperature coefficient of the non-explosive reaction between −104° and −77°, the activation energy appears to be 3·8 kg.-cal.[111-113]

The oxidation of hydrogen bromide by molecular oxygen between 490° and 635° is almost entirely a homogeneous reaction, the mechanism probably being:

$$\begin{aligned} HBr + O_2 &\rightarrow HOOBr \\ HOOBr + HBr &\rightarrow 2HOBr \\ HOBr + HBr &\rightarrow H_2O + Br_2. \end{aligned}$$

Added inert gases decrease the rate, probably by accelerating the decomposition of the intermediate complex HOOBr. The activation energy of the overall reaction, deduced from the variation in the rate with temperature, is 37·3 kg.-cal.[114] Atomic oxygen formed in a silent discharge oxidizes hydrogen bromide rapidly and completely; under the conditions of the experiment the absorption bands of the hydroxyl radical were not observed.[115,116] Atomic nitrogen and hydrogen bromide yield bromine, ammonium bromide and traces of other compounds.[117,118] An afterglow is observed only when the nitrogen is contaminated with oxygen or traces of oxygen-containing compounds; these phenomena appear to be connected with the presence of atomic bromine rather than with that of molecular hydrogen bromide.[118,119]

Hydrogen bromide also reacts rapidly with atomic hydrogen.[120-122] The thermal reactions with hydrogen at 821-984°K. and deuterium at 884°K. are chain processes involving hydrogen or deuterium atoms. For the reaction with hydrogen the mechanism is:

$$H_2 \rightarrow 2H \quad \ldots . (1)$$

$$H + HBr \rightarrow H_2 + Br \quad \ldots . (2)$$

$$Br + H_2 \rightarrow HBr + H \quad \ldots . (3)$$

The reaction with deuterium is similar.[121] A theoretical discussion of this reaction using transition state theory has been given, and it has been shown that agreement between theory and experiment is satisfactory.[121] The reactions of hydrogen atoms and methyl radicals (produced by photolysis of hydrogen iodide and methyl iodide) with hydrogen bromide have been interpreted to show that the velocity constant of the reaction $H + Br_2 \rightarrow HBr + Br$ is 8·4 times that of the reaction $H + HBr \rightarrow H_2 + Br$, and that the velocity constant of the reaction $CH_3 + I_2 \rightarrow CH_3I + I$ is $7{\cdot}5e^{950/RT}$ times that of the reaction $CH_3 + HBr \rightarrow CH_4 + Br$ at temperature T.[122]

Hydrogen bromide photosensitizes the hydrogen-oxygen reaction at 280°,[125] presumably owing to the more rapid formation of hydrogen atoms from this substance than from hydrogen. It is also reported to sensitize the oxidation of certain organic compounds under special conditions[126] and the reduction of ferric oxide by hydrogen.[127]

Hydrogen bromide reacts with ammonia even when both gases are liberated from intensively dried liquids at -80°;[128] the change in magnetic susceptibility during this reaction has been measured.[129] Crystalline silicon is perceptibly attacked by hydrogen bromide at 340°, and at 360° reaction is rapid, with the formation of $SiBr_4$, $SiHBr_3$ and a little SiH_2Br_2; at higher temperatures the tetrabromide is the main product.[130] There is no evidence for azeotrope or compound formation between hydrogen bromide and diborane[131] or boron trifluoride.[132]

The study of the effect of temperature and concentration on the oxidation of hydrobromic acid by sulphuric acid shows that appreciable oxidation takes place by 90% sulphuric acid at 35°, by 60% acid only at 170°.[133] Reduction of permanganate by hydrogen bromide takes place even in 0·00154 N. solution at room temperature.[134] The oxidation of hydrobromic acid by chromic acid has been investigated in some detail.[135-137] The rate of oxidation is a function of the concentrations of hydrogen and other ions. Chlorides accelerate the reaction, but retard it in the presence of sulphates. Manganous ions catalyse the oxidation. In the presence of sulphuric acid in low concentration the oxidation is said to be bimolecular, and at high concentrations of the acid unimolecular and independent of the concentration of the oxidising agent. Mechanisms have been suggested, but further experimental work is needed. The reduction of vanadic acid by hydrobromic acid in the presence of sulphuric acid has been studied in less detail: in this system, too, the concentration of sulphuric acid affects the rate in a complicated way, and if the acidity is too low the reaction stops.[138]

Hydrobromic acid reduces ruthenium tetroxide rapidly to quadrivalent ruthenium, and then slowly to the tervalent state; this reaction may be used for the determination of the element.[139] Tervalent ruthenium salts catalyse the oxidation of hydrobromic acid by perchloric acid, which, like many other oxidations by perchloric acid, is otherwise thermodynamically possible but exceedingly slow; the rate appears from a partial investigation to be proportional to the perchloric acid and tervalent ruthenium concentrations.[142] Osmium tetroxide is also reduced: in the presence of low concentrations of the acid and tribromide ion, Os^{VII} results; but with high concentrations of acid and low concentrations of bromide ion, the reduction proceeds as far as Os^{IV}.[140,141] In 1·2 – 3·5 M-acid the rate-determining step is reduction to Os^{VI}:

$$H_2OsO_5 + H^+ + Br^- \rightarrow H_2OsO_4 + HOBr$$

This is followed by rapid reactions:

$$\begin{aligned} HOBr + H^+ + Br^- &\rightarrow Br_2 + H_2O \\ Br_2 + Br^- &\rightarrow Br_3^- \\ H_2OsO_4 + \tfrac{1}{2}Br_3^- &\rightarrow HOsO_4 + H^+ + \tfrac{3}{2}Br^- \\ HOsO_4 + Br^- &\rightarrow Os\,(OH)O_3Br^{--} \end{aligned}$$

The overall reaction is:[141]

$$OsO_4 + H^+ + \tfrac{5}{2}Br^- \rightarrow Os(OH)O_3Br^- + \tfrac{1}{2}Br_3^-$$

The interaction of hydrogen peroxide and bromine or hydrobromic acid is discussed on page 717.

The rate equation for the oxidation of hydrobromic acid by chloric or iodic acid is given by

$$-\frac{d}{dt}\,[XO_3^-] = k[XO_3^-]^x\,[Br^-]^y[H^+]^z$$

where $x = y = 1$, $z = 2$ for chloric acid, and $x = 1$, $y = 2$, $z = 3$ for iodic acid.[143] The reaction with bromic acid is discussed on page 754; its velocity in aqueous solution at 1500 atm. pressure is reported to be about 15% less than that at 1 atm. pressure.[144]

At 25°, the rate of dissolution of aluminium (99·3% pure) in 0·5 – 4 N-hydrobromic acid is only slightly dependent on the velocity of stirring; it has a temperature coefficient of about 2 for a 10° rise in temperature, and it is greatly increased by adding aluminium chloride to the solution.[145] No modern explanation of these observations has apparently been given and further work with pure materials is required. Corrosion of calcium, zinc and beryllium has also been studied in an unsuccessful effort to correlate corrosion with the structures of the metals and with the products.[146] The effect of bromide in strong acid solutions in rendering iron passive has been ascribed to the formation of a protective film of ferric bromide.[147]

Hydrobromic acid in acetic acid slowly reacts with sulphur dioxide in a complex manner.[148] Formation of thionyl bromide,

$$SO_2 + 2HBr \rightarrow SOBr_2 + H_2O$$

is suggested as the first stage, followed by the reactions,

$$\begin{aligned} 2SOBr_2 + 4HBr &\rightarrow S_2Br_2 + Br_2 + 2H_2O \\ \text{and } Br_2 + SO_2 + 2H_2O &\rightarrow H_2SO_4 + 2HBr. \end{aligned}$$

Formation of sulphur from the disulphur dibromide also occurs; it is suggested that the bromide hydrolyses giving sulphuric acid and hydrogen sulphide, which then reacts with the sulphur dioxide. In the presence of acetyl bromide or acetic anhydride disulphur dibromide can be isolated and no hydrolysis of this compound occurs.

The extensive literature on the addition of hydrogen bromide to olefins is summarized in a review by Mayo and Walling.[149] Addition of hydrogen bromide is normally a polar process, the bromine attaching itself to positions of lowest electron density (*a*). but in the presence of peroxides an atomic mechanism (*b*) is believed to operate, and the direction of addition is reversed; e.g., with allyl bromide:-

$$CH_2{=}CH-CH_2Br \begin{array}{l} \nearrow (a)\ CH_3.CHBr.CH_2Br \\ \\ \searrow (b)\ CH_2Br.CH_2.CH_2Br \end{array}$$

Hydrogen bromide is unique among the hydrogen halides in this respect. The effect is observed both with liquid olefins and with their solutions.

Very accurate determinations of the heat of neutralization of hydrobromic acid at 20° in 0·01 M. solution have been made by Richards and his collaborators.[151,152] For neutralization with 0·01 M-lithium, sodium and potassium hydroxides the heats of neutralization were found to be 14·002, 13·836 and 13·981 kg.-cal., respectively.[151] The value for the neutralization of sodium hydroxide was later corrected (using the best available values for the specific heat of the solution) to 13·856 kg.-cal., the unit used being the 20° calorie.[152]

Below -75° hydrogen bromide combines with hydrogen chloride to form a compound, HBr,HCl; this is unstable in the vapour phase or in solution in hydrogen bromide or hydrogen chloride. Its vapour pressure between -120° and -80° is represented by the equation:-[153]

$$\log p = -\frac{811}{T} + 6{\cdot}818.$$

Nothing is known of its structure, and there is no direct evidence to support a suggested formulation[154] $H_2Cl^+Br^-$.

Molecular volume measurements provide evidence for the existence of a compound $(C_2H_5)_2O,2HBr$.[150]

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SECTION XXV

IODINE BROMIDE.

By A. G. SHARPE

The conclusion that there is only one bromide of iodine, IBr (Mellor, II, 122), remains unchallenged. Recent work on this compound has been concerned mainly with the determination of its physical properties; these have been reviewed by Greenwood.[1]

The structure of solid iodine bromide is unknown, but solid solutions of iodine and bromine over the range 0 – 38 mole-% Br_2 have been investigated by *X*-ray methods. In this range the lattice spacings vary linearly with composition; the solid solution belongs to the space group *Ccm*, and is thus isomorphous with iodine and bromine. This strongly suggests a molecular lattice with oriented iodine bromide molecules.[2]

In solvents in which iodine and iodine monochloride form violet and red-brown solutions respectively, iodine bromide forms red solutions; in solvents in which the colours of iodine and the monochloride solutions are respectively brown and yellow, solutions of iodine monobromide are yellow-orange. Solvents of the former class include carbon tetrachloride, chloroform, hexane, benzene, toluene, and carbon disulphide; those of the latter, methyl and ethyl alcohols, ethyl ether, formic and acetic acids, ethyl acetate, and acetone. These phenomena have been very much less investigated than those involving iodine or iodine monochloride, but it seems likely that Fairbrother's suggestion of polarization by co-ordination with an electron-donating atom in the second group of solvents may be applicable here.[3] In this connection the observation (Mellor, II, 124) that solutions of iodine bromide in carbon tetrachloride and ethyl ether are non-conducting and conducting, respectively, is significant. Addition of 1% of ethyl alcohol to the solution in carbon tetrachloride results in a marked lightening of the colour, and similarly the addition of a few drops of ether to the non-conducting solution in carbon disulphide produces a lighter solution which does conduct electricity. Such observations indicate partial formation of ionized complexes[1] such as $[(C_2H_5)_2O \rightarrow I]^+I^-$. The dipole moment of iodine bromide is reported to be 1·2 D. in benzene solution at 25°,[4] and 1·3 D. in carbon tetrachloride at 20°;[5] the value for the vapour is unknown.

From investigation of the equilibrium

$$CuBr_{2(s)} + \tfrac{1}{2}I_{2(g)} = CuBr_{(s)} + IBr_{(g)}$$

the equilibrium constant of the reaction

$$IBr_{(g)} = \tfrac{1}{2}I_{2(g)} + \tfrac{1}{2}Br_{2(g)} \qquad \ldots\ldots(1)$$

was evaluated as $8{\cdot}00 \times 10^{-2}$ at 115°, $9{\cdot}20 \times 10^{-2}$ at 151·2°, and $10{\cdot}01 \times 10^{-2}$ at 176°.[6] These values led to the equation

$$\Delta G^{\circ} = -1270 - 1{\cdot}7449\,T \text{ g.-cal.} \qquad \ldots\ldots(2)$$

for the free energy of formation of gaseous iodine bromide by the reverse of reaction (1).

An earlier determination of the equilibrium constant of reaction (1) at 304·8° was based on the effect of iodine on the formation of hydrogen bromide from hydrogen and bromine;[7] this gave a constant of 0·114 in moderate agreement with the value of 0·137 calculated from equation (2).[8] Vapour density determinations at 1495°K. gave 0·093 for the equilibrium constant of reaction (3):[6]

$$I_{2(g)} + Br_{2(g)} = 2IBr_{(g)} \qquad \ldots\ldots(3)$$

The change in heat content attending the formation of gaseous iodine bromide by the reverse of reaction (1) was calculated from the equilibrium constants to be -1270 ± 50 g.-cal.[8] (*see below*). The degree of dissociation of iodine bromide vapour at 25° was evaluated as 8·9%.[8]

Thermodynamic properties of iodine bromide were tabulated by McMorris and Yost,[8] and partly revised by Blair and Yost,[13] after publication of spectroscopic determinations of the heat of dissociation of iodine bromide.[9,10] These authors gave, for the reaction

$$\tfrac{1}{2}I_{2(s)} + \tfrac{1}{2}Br_{2(l)} = IBr_{(g)},$$

$$\Delta G^{\circ}_{298} = 971 \text{ g.-cal., and } \Delta H^{\circ}_{298} = 9{,}861 \text{ g.-cal.}$$

The standard entropy of gaseous iodine bromide was given as 62·0 g.-cal. $deg.^{-1}mole^{-1}$.

According to Greenwood,[1] re-evaluation of the spectroscopically determined heat of dissociation, using the latest values for the universal constants, leads to a value of 41·89 kg.-cal. for dissociation into normal atoms. This result, combined with the heats of dissociation of the halogens, gives

$$\Delta H^{\circ}_{298} = -1{\cdot}38 \text{ kg.-cal.}$$

for the reaction

$$\tfrac{1}{2}I_{2(g)} + \tfrac{1}{2}Br_{2(g)} = IBr_{(g)},$$

and

$$S^{\circ}_{298} = 62{\cdot}25 \text{ g.-cal.deg.}^{-1}\text{mole}^{-1}$$

for the standard entropy of gaseous iodine bromide.

Zeise[11] calculated the equilibrium constant for the last reaction in the range 298 – 2000° K. on the assumption that the internuclear distance in iodine bromide is the mean of the values in the parent halogens. For 400° K. he found $K_p = 11{\cdot}42$; the interpolated value from experimental results[8] is 11·9.

The partial pressure of iodine bromide above its solution in carbon tetrachloride obeys Henry's law at 25°, and if p = the v.p. of IBr in mm. and N = the mole fraction of IBr, $p/N = 114$ in the range $N = 0.00179$ to $N = 0.0224$; Hence ΔG° for the reaction

$$IBr_{(g)} = IBr_{(CCl_4)}$$

is -1124 g.-cal.[12] For the formation of iodine bromide in carbon tetrachloride by the reaction

$$\tfrac{1}{2}I_{2(s)} + \tfrac{1}{2}Br_{2(l)} = IBr_{(CCl_4)},$$

$\Delta G^{\circ}_{298} = -153$ g.-cal. and $\Delta H^{\circ}_{298} = 1721$ g.-cal. The standard entropy of iodine bromide in carbon tetrachloride is 38·5 g.-cal. $deg.^{-1}$ $mole^{-1}$.[13]

For the formation of iodine bromide from iodine and bromine dissolved in carbon tetrachloride, $\Delta H^{\circ}_{298} = -1630$ g.-cal., and for the solution of gaseous iodine bromide in carbon tetrachloride $\Delta H^{\circ}_{298} = -8140$ g.-cal.[13]

From absorption spectrum data, the degree of dissociation of iodine bromide in carbon tetrachloride has been found to be 5·9 ± 1.5%.[14]

In addition to earlier work, in which iodine bromide was shown to form conducting solutions in liquid sulphur dioxide, arsenic trichloride, and sulphuryl chloride (Mellor, II, 124), the formation of conducting solutions in bromine, nitrobenzene and acetic acid has also been reported.[17] The conductivity of a 14·83% solution in acetic acid at 25° is $1{\cdot}59 \times 10^{-5}$ ohm^{-1}cm.$^{-1}$; but neither in this solvent nor in bromine, sulphur dioxide, arsenic trichloride and nitrobenzene has any decomposition potential been found.[17] The decomposition potential at 15 – 18° of an aqueous solution containing 0·51 moles IBr/litre is 0·045 V.[18] A recent reinvestigation of the conductivity of fused iodine bromide gave values of $6{\cdot}4 \times 10^{-4}$ and $10{\cdot}4 \times 10^{-4}$ ohm^{-1}cm.$^{-1}$ at 45° and 55° respectively.[20] The value for the conductivity of the solid is wrongly transcribed in Mellor (II, 124); it is $6{\cdot}5 \times 10^{-6}$ ohm^{-1}cm.$^{-1}$ at 16·3°. This large difference between the conductivities in the solid and liquid states appears to establish the electrolytic nature of conduction in the liquid.

Iodine bromide dissolves in sulphur dioxide to give a solution containing approximately 6% of IBr at 25°.[21]

The reactions between molten iodine bromide and a large number of elements have been briefly reported.[29] Bromides insoluble in carbon tetrachloride, which is used to wash away iodine (formed as the other product of the reaction) and any excess of iodine bromide, are given by sodium, potassium, magnesium, calcium, barium, copper, silver, gold, zinc, mercury, tellurium, bismuth, manganese, iron, cobalt, and nickel. Bromides soluble in carbon tetrachloride are given by aluminium, germanium, tin, titanium, phosphorus, arsenic, antimony, vanadium, sulphur, and selenium. Cadmium, boron, carbon, silicon, lead, zirconium, niobium, tantalum, chromium, molybdenum, tungsten, and platinum do not react with molten bromide.

The interaction of solutions of iodine bromide and potassium iodide in fused iodine proceeds according to the equation:- $\mathrm{KI} + \mathrm{IBr} = \mathrm{KBr} + \mathrm{I_2}$ and may be followed conductometrically. On the solvent theory of acids and bases, iodine bromide is an acid in liquid iodine, in which it dissociates to give the free or solvated cation $\mathrm{I^+}$ characteristic of this solvent.[19]

In 0·05 M. solution in methyl alcohol, iodine bromide and silver nitrate react to form silver bromide and a pale yellow solution presumed to contain iodine nitrate:[22]

$$\mathrm{AgNO_3} + \mathrm{IBr} = \mathrm{AgBr} + \mathrm{INO_3}$$

The observation that in aromatic organic chemistry iodine bromide invariably acts as a brominating agent[23, 24] is accounted for by the high degree of thermal dissociation of the bromide and the rapidity of bromination by the free bromine formed.[24]

When iodine bromide in carbon tetrachloride is shaken with aqueous perchloric acid, the reaction

$$\mathrm{I_2} + 5\mathrm{Br_2} + 6\mathrm{H_2O} = 12\mathrm{H^+} + 2\mathrm{IO_3^-} + 10\mathrm{Br^-}$$

takes place between the free halogens present; the $\mathrm{Br^-}$ ions produced then extract iodine bromide to yield a solution containing $\mathrm{IBr_2^-}$ ions.[12] The distribution ratio IBr in $\mathrm{CCl_4}$/IBr in $\mathrm{H_2O}$ is reported to be 3·9;[15] the determination was made in the presence of sulphuric acid with the object of repressing hydrolysis, but its significance appears doubtful. The dissociation constant of the $\mathrm{IBr_2^-}$ ion,

$$\mathrm{IBr_2^-}_{(\mathrm{aq.})} = \mathrm{IBr}_{(\mathrm{aq.})} + \mathrm{Br^-}_{(\mathrm{aq.})}$$

has been given as approximately 0·003[12] and 0·0027.[15] Values of $1{\cdot}2 \times 10^{-5}$ and $1{\cdot}9 \times 10^{-5}$ in N- and 4N-hydrobromic acid respectively have been reported for the equilibrium constant of the dissociation $2\mathrm{IBr} = \mathrm{I_2} + \mathrm{Br_2}$ in aqueous solution; the higher value in more concentrated acid has received no satisfactory explanation.[15,16] The equilibria involved appear to be more complex than has previously been supposed. A study of the $IBr-Br_2-HBr$ system in aqueous solution suggests the possibility of the existence of an unstable IBr_4^- ion in the presence of bromine and hydrobromic acid,[16] but no salts containing such ions have ever been isolated in the solid state.

The conductivity of binary mixtures of fused iodine bromide and other molten halides has been investigated. The electrical conductivity of the system $IBr-KBr$ shows a maximum at 9 mole-% of KBr at 45°, that of $IBr-KI$ at 7 mole-% of KI at 45 – 55°, and that of $IBr-AlBr_3$ at 11 mole-% of $AlBr_3$ at 45 – 55°. Conductivities in iodine bromide resemble those in iodine chloride, but are generally rather lower. The viscosity of the $IBr-AlBr_3$ system is at a maximum at 55 mole-% $AlBr_3$, indicating the formation of a compound $IAlBr_4$.[20] On electrolysis of a solution of this compound in nitrobenzene, iodine migrates to the cathode, while aluminium and bromine migrate to the anode, suggesting the presence of I^+ and $AlBr_4^-$ ions; a little iodine also goes to the anode, probably because of the formation and electrolysis of the compound $[PhNO_2.I]^+ I^-$;[25] Ion transfer experiments on solutions of potassium dibromohypoiodite, $KIBr_2$, in the same solvent establish that iodine and bromine both accumulate at the anode.[25]

Iodine bromide and phosphorus tribromide react forming iodine and a compound $IPBr_6$; the latter substance may be obtained pure by fusing a mixture of 51 mole-% PBr_3 and 49 mole-% IBr, extracting with phosphorus tribromide, washing with carbon disulphide and drying in a stream of dry carbon dioxide at 50°.[26] A simpler method is to mix saturated solutions of phosphorus pentabromide and iodine bromide in carbon disulphide and to dry as before.[26] The m.p. of the compound $IPBr_6$ is 114·5°; electrolytic studies in nitrobenzene show that iodine migrates to the anode and phosphorus to the cathode, suggesting that the compound may be formulated as a salt, $PBr_4^+ IBr_2^-$.[27] This suggestion finds strong support in the recent demonstration that in the solid state the analogous compound $IPCl_6$ has a lattice made up of PCl_4^+ and ICl_2^- units.[28]

Molten iodine bromide as an ionizing solvent has been briefly discussed by Gutmann.[30] Solutions of alkali metal bromides are good conductors, those of bromides of antimony, zinc, tin (stannic), and aluminium are moderate conductors. In this solvent, the compound $PBr_4^+IBr_2^-$ behaves as a base; and reactions of the type

$$2MIBr_2 + SnBr_4 \rightarrow M_2SnBr_6 + 2IBr$$

(where M = K, NH_4, Rb, Cs) have been shown to take place. The existence of stable acids in the iodine bromide-solvent system has not yet been established.

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SECTION XXVI

BROMINE OXIDES AND OXY-ACIDS

By A. G. SHARPE and B. COX

OXIDES OF BROMINE

By A. G. SHARPE

BROMINE MONOXIDE Br_2O.

A reinvestigation of the interaction of bromine and mercuric oxide (Mellor, II, 242) showed that when bromine vapour was passed at 50 - 60° over the oxide (precipitated at 50° and dried at 100 - 110°), about 4% of bromine monoxide was formed.[1] Better results were obtained by shaking the oxide with a solution of bromine in carbon tetrachloride.[2,3] In one process,[3] mercuric oxide (15 g.) was shaken with bromine (5·3 g.) in carbon tetrachloride (90 cc.) at 45° for 45 min.; more mercuric oxide (20 g.) was then added, and shaking was continued for 4½ hr. at -18°. The yield of bromine monoxide in the organic solvent (40 - 50%, based on the weight of bromine taken) was determined iodometrically, one molecule of the monoxide liberating four atoms of iodine from potassium iodide solution.

The first product in the reaction between bromine and mercuric oxide is an unstable compound, $HgOBr_2$, which rapidly decomposes into mercuric hypobromite and bromide:[3,11-13]

$$2HgOBr_2 \rightarrow Hg(OBr)_2 + HgBr_2.$$

In carbon tetrachloride solution, bromine then reacts thus:

$$Hg(OBr)_2 + Br_2 \rightarrow Br_2O + HgOBr_2.$$

In the absence of such a solvent, the oxide reacts further with unchanged hypobromite, producing bromine and mercuric bromate:-[13]

$$Hg(OBr)_2 + 4Br_2O = 4Br_2 + Hg(BrO_3)_2.$$

Pure bromine monoxide has been prepared in 7 - 10% yield by decomposition of the dioxide in vacuo at temperatures above -40°, bromine, which was also formed, being removed by fractional sublimation.[4,5] The formula of the monoxide was determined by thermal decomposition into bromine and oxygen, and by a cryoscopic determination of its molecular weight in carbon tetrachloride.

Bromine monoxide is a brown solid, m.p. -17·5 ± 0·5° with some decomposition; it is stable only below -40°.[5] Its green solution in carbon tetrachloride decomposes rapidly in light, slowly in the dark, $2Br_2O \rightarrow 2Br_2 + O_2$; $Br_2O + CCl_4 \rightarrow COCl_2 + Br_2 + Cl_2$.[2,4] The extinction coefficients of bromine monoxide in 26·3% solution in carbon tetrachloride are:[3]

Wave-length	430	470	500	530	570	610	660	720	750mμ.
ϵ	80·2	28·5	14·5	6·7	6·9	10·2	12·3	3·9	2·5

Treatment of the solution in carbon tetrachloride with sodium hydroxide solution at 0° gives only sodium hypobromite; the more vigorous direct decomposition of the gas by aqueous sodium hydroxide results in the simultaneous formation of some bromate.[5] Bromine monoxide dissolves in water to yield hypobromous acid, which then decomposes.[3]

TRIBROMINE OCTOXIDE Br_3O_8.

In an investigation of the decomposition of ozone by bromine, Lewis and Schumacher[6] noticed that after the gases were mixed a white deposit appeared on the walls of the containing vessel. By allowing pure bromine at 3 - 15 mm. pressure to react with 5 - 15 times as much pure ozone at -5° to +10°, bromine octoxide was obtained as a white flocculent solid, unstable except below -80° or in the presence of ozone.[7,9] Failure to adhere to these experimental conditions led to severe explosions.[9] Thermal decomposition of the oxide into bromine and oxygen served for its analysis; determination of its molecular weight was not possible.

Bromine octoxide is dimorphous, the more stable modification being obtained as fine white needles by prolonged cooling at -40°.[7,9] The transition temperature is -35 ± 3°. It dissolves in water to form a colourless solution which contains no bromide ions.[7] Iodometric and acidimetric determinations on the solution indicate a $Br:H^+$: active O ratio of 1:1·34:2·48. These values have been interpreted[7] as indicating that the solution contains an unstable acid, $H_4Br_3O_{10}$, but there is no further evidence to support this suggestion.

Below 15° the decomposition of ozone in the presence of bromine appears to involve this oxide. For low concentrations of bromine the rate of decomposition (a first order reaction occurring in the solid phase) is reported to be proportional to the first power of the concentration of the added bromine and to be independent of the nature and size of the reaction vessel, the presence of added oxygen and the pressure of ozone. These results indicate that the rate-determining step is the decomposition of the solid oxide; at 0° the temperature coefficient is 3·16 for 10° and the activation energy is 17·6 kg.-cal.[9,10,14] Both modifications of the oxide are equally effective in promoting the decomposition of ozone.[9] More extensive investigations of the kinetics of the decomposition indicate, however, that the reaction is more complex than the above account suggests: starting with bromine at 1 mm. and ozone at 15 - 50 mm. pressure, Lewis and Feitknecht[15] found that in this concentration range the rate is reduced by increasing the pressure of the ozone. A satisfactory general account of the reaction has not yet been given.

BROMINE DIOXIDE $(BrO_2)_x$.

This oxide was obtained in 80% yield by the action of an electric discharge on a mixture of bromine vapour and oxygen cooled to the temperature of liquid air; ozone and bromine were removed by fractional sublimation, leaving the dioxide as a yellow solid which when heated to 0° under atmospheric pressure decomposed into bromine and oxygen without first melting.[8] The preparation from atomic oxygen and bromine under similar conditions has also been reported by workers on atomic oxygen.[16,17]

Bromine dioxide is stable at -40°; if it is allowed to warm rapidly, it decomposes with visible flame.[5] It is decomposed by carbon tetrachloride, petroleum ether, or water; with water a colourless solution of unestablished composition results.[3] With cold aqueous 2N-sodium hydroxide, sodium bromide, hypobromite, bromite and bromate are formed; if the oxide is decomposed with 5N-sodium hydroxide and the solution is warmed, the course of the overall reaction can be represented thus:-[5]

$$6BrO_2 + 6NaOH \rightarrow 5NaBrO_3 + NaBr + 3H_2O$$

When bromine dioxide decomposes in vacuo, bromine monoxide and a white solid stable at -70° are formed;[4,5] it has been suggested that the latter substance is a new oxide, Br_2O_5, Br_2O_6, or Br_2O_7,[4,5] but the possibility that it is the oxide Br_3O_8 does not appear to have been eliminated.

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OXYACIDS OF BROMINE AND THEIR SALTS

By B. COX

HYPOBROMOUS ACID

All methods of any importance for the preparation of hypobromous acid solutions depend on disturbing the equilibrium

$$Br_2 + H_2O \rightleftharpoons HBr + HOBr$$

by adding a substance (*e.g.*, mercuric oxide, argentous oxide, mercuric nitrate, silver nitrate) which will remove bromide ions. Interaction of bromine water and silver nitrate solution,

$$AgNO_3 + Br_2 + H_2O \rightarrow AgBr + HNO_3 + HOBr,$$

followed by distillation at 20–25° under a pressure of 11–12 mm., yields a solution of concentration 0·3 N. containing very little nitric acid. Bromine and bromic acid are the only impurities present; the former may be removed by blowing a current of nitrogen through the solution, but removal of the bromic acid is impossible.[1] Silver phosphate may replace silver nitrate: bromine water is shaken with excess of silver phosphate until the odour of bromine disappears, and the solution is then distilled in all-glass apparatus.[198] A dilute solution of hypobromous acid has also been prepared by shaking excess of bromine water with silver nitrate solution, filtering off the silver bromide on glass wool, and removing the excess of bromine by blowing air through the filtrate.[2] Alternatively, excess of silver nitrate may be used, the excess of silver being removed by adding sodium phosphate.[3]

On standing, solutions of hypobromous acid decompose to bromic acid and bromine; under certain conditions bromous acid may be formed as an intermediate.[1-3] In the presence of low concentrations of bromide ion, the time for half-decomposition of hypobromous acid is about 10^7 times as great as that calculated from an earlier expression[199] for the rate law of the reaction

$$5HBrO \rightarrow BrO_3^- + H^+ + 2Br_2 + 2H_2O.$$

Re-examination of the experimental data on which this rate law was founded suggested that except in strongly alkaline solution the rate is proportional to $[HOBr]^2[BrO^-]$, the rate-determining step being the reaction

$$2HOBr + OBr^- \rightarrow BrO_3^- + 2Br^- + 2H^+;$$

this is followed by rapid interaction of bromide and bromate.[4] From an examination of earlier work, it is suggested[4] that in strongly alkaline media the rate determining step is:

$$2BrO^- \rightarrow BrO_2^- + Br^-.$$

By rewriting the expression for the decomposition in the form:

$$\frac{d}{dt}[HBrO] = k_1[HBrO]^3[OH^-],$$

it is seen that the reaction should be of the third order with respect to the hypobromous acid concentration at constant pH. In the pH range 6·4–7·8 at 25° this has been found to be so, and $k_1 = 4{\cdot}4 \times 10^8$ (concentrations in moles/litre, time in min.).[5] At pH 9 and in more alkaline solutions the order decreases to two.[5,6,74,140] Alternative expressions for the rate in nearly neutral media are

$$\frac{d}{dt}[HBrO] = k_2[HBrO]^2[BrO^-]$$

$$\text{and}\quad \frac{d}{dt}[\mathrm{HBrO}] = k_3[\mathrm{Br}_3^-]^3[\mathrm{OH}^-]^4/[\mathrm{Br}^-]^6$$

with $k_2 = 175{\cdot}5$ and $k_3 = 2{\cdot}1 \times 10^{22}$ respectively (units as above).[5]

The first determination of the dissociation constant of hypobromous acid at 20° gave a value of $2{\cdot}5 \times 10^{-8}$,[140] but this was deduced indirectly from a study of the effect of pH on the decomposition of hypobromous acid, and cannot be considered more than a rough value. Electrometric titration of hypobromous acid with sodium hydroxide, using the glass electrode, gave 2·06 and $2{\cdot}1 \times 10^{-9}$ at 20° and 22° respectively.[7,8] These determinations have been criticized on the grounds that the neutralization is complicated by the formation of some bromate,[11] but the latest investigation indicates that the criticism is probably invalid. By measuring the change in pH (using the glass electrode) when hypochlorite solutions of pH between 7·21 and 8·09 reacted quantitatively with bromide, and by assuming pK for hypochlorous acid to be 7·45, pK for hypobromous acid at 19° was determined as 8·70.[9] Electrometric titration against sodium hydroxide gives the dissociation constant at 5° as $1{\cdot}0 \times 10^{-9}$.[10] The dissociation constants of hypohalous acids and a large number of other acids have been discussed briefly by McGowan.[12] This author's value[12] of $\Delta G^\circ_{298} = +\,11{\cdot}8$ kg.-cal. for the dissociation of hypobromous acid is based on an unspecified source; the value given above for 20° corresponds to $\Delta G^\circ_{293} = +\,11{\cdot}9$ kg.-cal.

Investigation of the hypobromite–bromide formal oxidation–reduction potential in 1–5N-sodium hydroxide shows that the potential varies by no more than 0·05V. over this range of alkalinity.[13] Hypobromites strongly catalyze the hydration of carbon dioxide;[14] how they act is not known. The oxidation of ammonium ion by bromine,

$$2\mathrm{NH}_4^+ + 3\mathrm{Br}_2 \rightarrow 6\mathrm{Br}^- + \mathrm{N}_2 + 8\mathrm{H}^+,$$

is believed to be due to the intermediate formation of hypobromous acid. This oxidizes ammonium ions much more readily than does molecular bromine; slight decomposition, with liberation of oxygen, takes place simultaneously, and the quantity of bromine consumed is therefore slightly greater than that indicated by the above equation.[29] Evidence for the existence of positive bromine ions in solutions of hypobromous acid is discussed on page 713.

HYPOBROMITES

A solution of sodium hypobromite suitable for the determination of urea may be prepared by adding 1 cc. of concentrated hydrochloric acid to 5·5 cc. of a solution containing 6 g. of sodium bromate and 20·5 g. of sodium bromide in 100 cc. of water; the solution is shaken and set aside for several minutes, after which addition of 3·5 cc. of 30% sodium hydroxide solution produces 10 cc. of reagent.[15] Alternatively, 4 cc. of a 3N. solution of potassium bromate containing 10% by volume of sulphuric acid is slowly added, with stirring and cooling, to an equal volume of 3N-potassium bromide solution; 4 cc. of 6N-sodium hydroxide is added, and after shaking, the precipitated potassium hydrogen sulphate is allowed to settle and the clear solution is decanted off.[16]

The stabilization of sodium hypobromite solutions by excess of sodium hydroxide has been investigated at different temperatures; addition of alkali in quantities greater than 50% excess has little effect.[17] The decomposition is powerfully catalyzed by cupric ions, even in concentrations of the order likely to be present as an impurity in sodium hydroxide: in the presence of 10 p.p.m. of copper, 42% of a sodium hypobromite solution (of unspecified concentration) decomposed in 24 hours at 36–37°.[18] This result may be compared with a half-life of 20 hours at 30–35° for a 2N-hypobromite solution containing a 50% excess of sodium hydroxide;[17] in this experiment, however, no attempt to remove or detect traces of copper was made. Solutions of other alkali metal hypobromites are also stabilized by the presence of excess of alkali.[24] For biochemical purposes the deterioration of sodium hypobromite solutions stored in amber bottles is not serious in less than ten days at 18° or thirty days at 4°.[19]

The oxidation of mercuric cyanide by sodium hypobromite, the overall interaction being expressed by the scheme:

$$Hg(CN)_2 + 2NaOBr + 2NaOH \rightarrow HgO + 2NaBr + 2NaCNO + H_2O$$

has been variously suggested to involve direct oxidation of the undissociated cyanide to cyanate,[20] and the reaction sequence:-[21]

$$Hg(CN)_2 + 4NaBr \rightarrow Na_2HgBr_4 + 2NaCN$$

$$2NaCN + 2NaOBr \rightarrow 2NaCNO + 2NaBr$$

$$Na_2HgBr_4 + 2NaOH \rightarrow HgO + 4NaBr + H_2O.$$

A satisfactory discussion, which would involve knowledge of the instability constants of the complex ions involved, has not yet been given.

Sodium hypobromite reacts with hydrogen peroxide according to the equation

$$NaBrO + H_2O_2 = NaBr + H_2O + O_2,$$

and has been used for the removal of hydrogen peroxide in studies on the rates of hydrolysis of peroxy-compounds.[22] Sulphide is quantitatively oxidized to sulphate by excess of sodium hypobromite in the presence of 2·5 N-sodium hydroxide:

$$4BrO^- + S^{--} = 4Br^- + SO_4^{--}.$$

The excess of hypobromite is conveniently determined iodometrically.[199] Iodide is oxidized to iodate by alkaline hypobromite,

$$I^- + 3BrO^- = IO_3^- + 3Br^-,$$

and the excess of hypobromite may be determined by potentiometric titration with arsenite.[71] For accurate volumetric work it is recommended that hypobromite solutions should be standardized twice daily.[71] Sodium thiosulphate solution, when run into an excess of potassium hypobromite, is quantitatively converted into sulphate; if the thiosulphate is present in excess some hydrogen sulphide is formed.[25]

Magnesium hypobromite is obtained in solution by the action of bromine on a suspension of magnesium hydroxide; it is unstable in light or above 40°. It is inferred from its action on certain aromatic alcohols that magnesium hypobromite is a more powerful oxidizing agent than the sodium salt.[27] The stability of the solution remaining after treatment of bromine water with excess of solutions of silver salts depends on the silver salt used, *e.g.*, the solution remaining after the interaction of bromine and silver acetate decomposes more rapidly than that produced from bromine and silver nitrate.[26] These results are probably connected with the stability of bromine cations (page 713) in the presence of different anions.

A basic hypobromite having bactericidal and bleaching properties has been prepared by treating slaked lime with bromine (yielding a dark red compound of formula $CaOBr_2,H_2O$), and heating the product at 100–105° until it becomes light yellow in colour.[28] Strontium hydroxide monohydrate reacts with bromine vapour forming a product which contains bromide and hypobromite; after exposure to moist air, however, only bromide and bromate are present. With bromine in carbon tetrachloride, strontium hydroxide octahydrate yields appreciable amounts of hypobromite, but with bromine vapour only bromide and bromate are formed.[75]

The interaction of mercuric oxide and bromine is discussed in detail elsewhere (see page 747).

BROMOUS ACID AND BROMITES

The formation of bromous acid as an intermediate in the decomposition of hypobromous acid made from bromine and silver nitrate solutions has been demonstrated by determining the oxidizing power of the solution towards arsenite in the presence of bicarbonate and acidified iodide, and the total bromine content.[2] Hypobromite and bromite (but not bromate) oxidize arsenite in the cold; all three oxy-ions oxidize acidified potassium iodide solution. In these oxidations bromite is reduced to bromide:

$$BrO_2^- + 4H^+ + 4e = Br^- + 2H_2O.$$

The formation of bromous acid in dilute solutions in the absence of a large excess of silver salt has been confirmed; when hypobromous acid solutions are allowed to decompose, the concentration of bromous acid present rises during the first few hours and then drops, becoming zero in 150 hours at room temperature.[3]

Very little is known about the physical or chemical properties of bromous acid, and no solid bromite has yet been prepared.

BROMIC ACID AND BROMATES

Alkali metal bromates may be produced by a continuous electrolytic process from an aqueous solution containing the alkali metal bromide and an alkali metal chromate as a depolarizer, the resulting bromate being substantially free from discolouration due to the chromate.[30,31] The alkali metal hydroxide produced at the cathode is allowed to mix with the halogen produced at the anode and the solution is recirculated, the temperature being allowed to rise sufficiently to keep the bromate in solution; on allowing the solution to cool the bromate crystallizes out. To obtain colourless bromate from material contaminated with chromate, the compound in solution should be treated with metallic zinc before crystallization.[32]

The diamagnetic susceptibility of the bromate ion is variously reported as $39{\cdot}7 \times 10^{-6}$,[33,34] and $34{\cdot}1 \times 10^{-6}$ c.g.s. units.[35]

The viscosities of solutions of bromic acid and of mixtures of bromic acid with sodium and potassium bromates have been determined in the concentration range 0–2N. and for temperatures between 8° and 25°C.[36] and are presented in the form of viscometric titrations of sodium and potassium hydroxides with bromic acid. The apparent molal volume of the bromate ion in aqueous solution at infinite dilution and 25° is reported to be 36·4c.c. per g. ion; the corresponding value for the bromate ion in solid potassium bromate is 51·1 c.c. per g. ion.[37] The average value for the conductivity of the bromate ion at infinite dilution and 25° is 55·8 ohm^{-1}cm^2.[40,128] The absolute ionic velocity of the bromate ion at 18°, measured by means of Whetham and Nernst's ionic transport apparatus, is given in Table I.[39]

TABLE I. - ABSOLUTE IONIC VELOCITY OF BROMATE ION AT 18°

Normality	$^1/_4$	$^1/_{16}$	$^1/_{64}$	$^1/_{256}$	$^1/_{1024}$
$V \times 10^7$ cm./sec.	356·5	404·1	430·1	448·7	459·1

Bromates are insoluble in absolute acetone, except for lithium bromate which is slightly soluble, the solubility decreasing with temperature.[140] A value for the anisotropy coefficient of the bromate ion in solution, obtained from the Rayleigh scattering, is given as 15×10^{-3}. This compares with 24×10^{-3} for the nitrate ion and 75×10^{-3} for the carbonate ion.[38] The heat of hydration of the bromate ion (relative to $K^+ = 74$ kg.-cal.) is reported as 74 kg.-cal.g.-ion^{-1}.[41] It is reported that there is no exchange of radiobromine between bromide and bromate; this is in agreement with results obtained for other oxy-ions.[42]

The reaction of bromic acid with hydrobromic acid is represented by the scheme:

$$BrO_3^- + 5Br^+ + 6H^+ \rightarrow 3Br_2 + 3H_2O.$$

The rate-determining step is

$$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HBrO.$$

In accordance with this, at high concentrations and in the presence of excess hydrogen ions the reaction is found to be of second order and the rate is given by:[46]

$$-\frac{d}{dt}[BrO_3^-] = [BrO_3^-][H^+]^2\{300[Br^-]+34[Br^-]^2\}$$

The oxidation of arsenious acid by bromic acid in the presence of excess of hydrogen ions is a second order reaction and is autocatalytic with an induction period. The accelerating factor is bromide ion, and it appears that the arsenite is oxidized by the products of the reaction between bromic and hydrobromic acids. The initial production of hydrobromic acid must, however, be due to the interaction of arsenious and bromic acids. The effect of adding other acids to the reacting mixture is proportional to $[H^+]^2$; but with the halogen acids there is, as would be expected, a double effect due to the simultaneous addition of halide and hydrogen ions.[44-47]

At low concentrations the reaction between bromic and hydrobromic acids is of the fourth order and the rate law at 25° is given as:

$$-\frac{d}{dt}[BrO_3^-] = [BrO_3^-][H^+]^2\{300[Br^-]\}.$$

In the presence of perchloric or sulphuric acid solutions at 25°, where the total ionic strength is less than 0·2, the rate is given by:

$$-\frac{d}{dt}[BrO_3^-] = 540 \pm 15\,[BrO_3^-][H^+]^2[Br^-]\gamma^4_{HBr}.$$

In this case the energy of activation is 16·0 ± 0·3 kg.-cal., and by the introduction of the activity coefficient the values of k for sulphuric acid solutions agree with those for perchloric acid solutions.[46,52]

In the presence of phenol the reaction

$$BrO_3^- + 2Br^- + 3H^+ \rightarrow 3HBrO$$

occurs with measurable velocity, in addition to

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O,$$

and there is direct oxidation-reduction between bromic acid and phenol.[48] At low concentration ($[H^+] < 0{\cdot}4$N.) the autocatalytic reaction between bromate and hydrogen peroxide proceeds according to the scheme:

$$BrO_3^- + 3H_2O_2 \rightarrow Br^- + 3H_2O + 3O_2.$$

Results for the reaction at 25° in the dark agree well with:

$$-\frac{d}{dt}[BrO_3^-] = k_1[BrO_3^-][H_2O_2][H^+] + k_2[BrO_3^-][Br^-][H^+]^2,$$

where $k_1 = 0{\cdot}026 \pm 0{\cdot}004$ and $k_2 = 99 \pm 2$ for the reaction in 0·12 N-sulphuric acid.[49]

In the oxidation of phosphorous acid by potassium bromate the induction period is approximately inversely proportional to the concentration of either reagent, decreases with rise in temperature or with the addition of *iso*propyl alcohol, and increases with the addition of *n*-propyl alcohol; it is unaffected by cations, is decreased by maleic, *d*-tartaric and *l*-tartaric acids and increased by fumaric acid.[50] The analogous reaction between bromate and hypophosphorous acid shows similar variations in the induction period. This varies inversely as the concentration of either of the reactants and is diminished by rise in temperature or by the addition of methyl, ethyl and *iso*propyl alcohols or glycerol; *n*-butyl and *iso*propyl alcohols shorten the induction period to about the same extent. Sulphate ion and also *n*-propyl alcohol increase the induction period, whereas chloride, bromide, thiosulphate, thiocyanate, dithionate and collodial sulphur sols reduce it greatly.[51]

The reaction between bromate and deuterium iodide in 95% D_2O has been studied and is found to be somewhat faster than the analogous reaction with hydriodic acid.[53]

The reaction of chromium sesquioxide with alkali halate is autocatalytic and proceeds according to the scheme:

$$5Cr_2O_3 + 6KBrO_3 + aq. \rightarrow 3K_2Cr_2O_7 + 4CrO_3,aq. + 3Br_2.$$

The reaction is apparently catalysed by hydrogen ion and although it does not go to completion at 18° is very rapid at 100°. The reaction is retarded by adding bromide and is stopped completely by the removal of hydrogen ion, for example by alkalis or alkali carbonates. Thus chromium sesquioxide, potassium bromate and calcium carbonate heated under reflux do not liberate any bromine.[54-56]

The reaction between potassium bromate and sodium nitrite in aqueous solution acidified with potassium bisulphate proceeds according to the equation:

$$\text{Rate} = [k_1 + k_2(S)^2][BrO_3^-]^2,$$

where S is the concentration of acid, k_1 is the velocity coefficient for the unaccelerated reaction between bromate and nitrous acid and k_2 the acceleration coefficient of the reaction by acid.[57] The reaction is unaffected by changing the bromide ion concentration.[58]

The reduction potential of 0·001 N-bromate solution at a dropping mercury electrode in 0·1 N. solutions of electrolytes is −1·66 V. in the presence of univalent cations (Na, K), −1·31 V. for bivalent cations (Ca, Sr, Ba) and −0·63 V. for the trivalent cation, La. In acid solution the value is −0·16 V. Bromate ion can be determined by the polarographic method in the presence of chlorate, iodate, nitrate and nitrite.[59] The waves produced by the polarographic reduction of bromate in acidic, neutral and alkaline solution have been studied and the reduction is irreversible; the relation between the potential, the value of $\frac{i_d - i}{i}$, and the concentration of the cation (M) is given by:-[60-62]

$$\pi = \pi_{1/2} + a \log \left(\frac{i_d - i}{i}\right) + b \log M.$$

No satisfactory explanation has been given of the catalysis of the reaction between silver and bromic acid by ferric sulphate.[63]

In boiling acids there is no appreciable decomposition of potassium bromate in 5 minutes for solutions of 0·025 N-potassium bromate in 0·3 N-perchloric, nitric or acetic acids; it is less stable in sulphuric and phosphoric acids. For determining small concentrations of bromide as impurity in samples of potassium bromate, however, the slight decomposition which does occur on boiling with sulphuric or nitric acids may liberate as much bromine as is liberated by the trace of bromide present as impurity, thus rendering the method unreliable.[64,65] Potassium bromate is highly suitable for use as a primary standard in volumetric analysis;[67] bromate–bromide standard solutions may be prepared directly by weighing or may be standardized against arsenious oxide or standard sodium thiosulphate solution.[66]

In liquid hydrogen fluoride, bromates react with the evolution of bromine and oxygen.[68] With bromine trifluoride, bromates evolve oxygen quantitatively and are converted into fluorides or bromofluorides.[69]

Leucofluorescein may be used as a reagent for detecting traces of oxidizing agents; the sensitivity is 4·5γ for bromate ion and the limiting dilution 1 in 7 × 10^5 in acidic solution.[70]

Refs. p. 770

The adsorption of bromate ions on alumina, ferric oxide and chromium sesquioxide has been investigated and the order of adsorption of anions is given as follows:-[72,73]

On Al_2O_3 : $CNS^- \geq NO_3^- > BrO_3^- > IO_3^- > Fe(CN)_6^{4-} > C_2O_4^{--}$

On Fe_2O_3: $CNS^- > BrO_3^- > CN^- > CrO_4^{--} > IO_3^- > NO_3^-$

On Cr_2O_3 : $BrO_3^- > IO_3^- > NO_3^- > CrO_4^{--} > CNS^- > CN^-$

LITHIUM BROMATE

The solubility of lithium bromate in water has been measured in the temperature range -45° to 143° and the relative viscosity determined for concentrations of 10-50%. Below 52° the stable phase is the monohydrate and above 52° it is the anhydrous salt. The transition point obtained from a series of results is 50·8°. The solubility is given in Table II.

TABLE II. - SOLUBILITY OF LITHIUM BROMATE IN WATER

t°	5	15	25	35	50	53	56	70·5	85	100
g./100 g. sat. soln.	61·6	63·3	65·4	67·5	71·5	72·4	72·6	74·3	76·2	78·0
stable phase	← $LiBrO_3.H_2O$ →					← $LiBrO_3$ →				

The saturated solution at 143° contains 84·6% of anhydrous salt. A eutectic is formed at -47° and contains 54·5% of the anhydrous salt. Lithium bromate readily forms supersaturated solutions which remain as syrups down to -70°. It melts at 248° with some decomposition; extrapolation of the solubility curve, however, would indicate a melting point of 260°.

Anhydrous lithium bromate forms crystals belonging to the rhombic or monoclinic systems; the monohydrate crystallises in the rhombic system.

A solution of lithium bromate, saturated at room temperature, cooled to -50° for several hours, and allowed to warm to room temperature slowly, contains a crystalline deposit of the dihydrate; this loses water when heated above 60 - 70°.[76,77]

The molar magnetic susceptibility of lithium bromate, measured on the solid, is -39×10^{-6} c.g.s. units and measured in aqueous solution is $-38{\cdot}7 \times 10^{-6}$ c.g.s. units.[35]

SODIUM BROMATE

The solubility of sodium bromate has been measured between 5° and 100°.[78,108] The values obtained[108] are given in Table III.

TABLE III. - SOLUBILITY OF SODIUM BROMATE IN WATER

t°	5	10	15	20	25	30	35	40	50	100
density of sat. soln.	1·194	1·211	1·232	1·248	1·257	1·284	1·288	1·310	—	—
g./100 g. sat. soln.	21·42	23·24	24·94	26·69	28·29	29·85	31·35	32·8	35·55	47·6

Jones and Froning obtained a value 2·612 moles/l. for the solubility at 25° by Scatchard's method:[78] this compares with 2·615 moles/l. obtained from Ricci's results.[108]

In a water-deuterium oxide mixture containing 91·59% D_2O the solubility of sodium bromate at 5° is 2·899 moles/100 moles solvent.[79] In liquid sulphur dioxide at 50° under pressure sodium bromate is only slightly soluble (between 0·01 and 0·1%).[80]

The elastic constants of the sodium bromate crystal have been measured[81] and are quoted in Table IV.

TABLE IV. - ELASTIC CONSTANTS OF CRYSTALLINE SODIUM BROMATE

	C_{11}	C_{12}	C_{44}	S_{11}	S_{12}	S_{44}	β
	$\times 10^{-11}$ dyne, cm.$^{-2}$			$\times 10^{13}$ cm.^{2} dyne^{-1}			
Bridgman and Mason	6·16	2·356	1·54	20·6	−5·7	65·0	27·6
Sundara Rao	5·45	1·91	1·50	22·4	−5·8	66·7	32·4

The compressibility of sodium bromate up to 25,000 kg./sq.cm. has been measured at 30° and 75°:-

TABLE V. - COMPRESSIBILITY OF SODIUM BROMATE

$\Delta v/v_0$	0·0071	0·0171	0·0320	0·0450	0·0567	0·0673
Pressure kg./cm.^{2}	2000	5000	10,000	15,000	20,000	25,000

Measurements have also been made in which hydrostatic pressures of up to 50,000 kg./sq.cm. have been combined with shearing stresses to the point of plastic flow.[92-94]

Sodium bromate shows a piezoelectric effect which has been measured in the temperature range 28°-240°.[83] The temperature coefficient of the piezoelectric constant is found to be about one hundred times that of the coefficient of thermal expansion, which is given as 28·6 × 10^{-6}.[82] This is much lower than other values quoted:-[84,90]

$t°$	−40 to 0°	0° to 50°	36·5°	50° to 90°	285·3°
coefficient	37·5 × 10^{-6}	39·2 × 10^{-6}	39·2 × 10^{-6}	41·7 × 10^{-6}	47·24 × 10^{-6}
reference	84	84	90	84	90

The thermal expansion may be represented by the equation[84]

$$\Delta l/l = a(t-25) + b(t-25)^2$$

where $a = 3{\cdot}94 \times 10^{-5}$; $b = 1{\cdot}0 \times 10^{-8}$.

The dielectric and piezoelectric constants of sodium bromate, measured on the solid, have been presented graphically, and the dielectric constant is given by the equation:[84]

$$\kappa = 4{\cdot}87 + \left(\frac{323}{414-T}\right).$$

By high frequency measurements in dilute aqueous solutions a value of 45 is obtained for the dielectric constant.[85] For the magnetic birefringence in concentrated solution a value of −0·11 has been quoted for sodium bromate, after correcting for the diamagnetism of the solvent.[86]

The atomic arrangement in the optically active crystal of sodium bromate has been discussed with reference to the theory of Born.[87,88] The magnetic rotation of the plane of polarisation (Faraday effect) has been measured at 0° for $\lambda = 546\,m\mu$:[89] the value obtained for the Verdet constant is 0·0175 min. of arc and the molar rotation (relative to H_2O = 1·0) is 6·21.[89]

The entropy of sodium bromate under standard conditions has been estimated[91] as $S^\circ_{298} = 31{\cdot}7 \pm 1{\cdot}0$g.-cal.deg.$^{-1}$ mole^{-1}

The conductivity, osmotic coefficients and activity coefficients of sodium bromate in solution at 25° have been determined as follows (see Table VI and Table VII).

TABLE VI. - EQUIVALENT CONDUCTIVITY OF SODIUM BROMATE IN SOLUTION AT 25°.[40]

moles $NaBrO_3$/l.	0·000508	0·001053	0·010836	0·05728	0·1058	0·4819
equiv. cond.	104·12	103·28	97·97	89·97	85·93	75·07

TABLE VII. - OSMOTIC AND ACTIVITY COEFFICIENTS OF SODIUM BROMATE IN SOLUTION AT 25°.[78,95]

moles $NaBrO_3$/l.	0·1	0·2	0·3	0·5	1·0	1·6	2·0	2·5
osmotic coefficient (ϕ)	0·918	0·896	0·883	0·865	0·833	0·808	0·800	0·792
activity coefficient (y)	0·758	0·696	0·657	0·605	0·528	0·473	0·450	0·426

The dissociation constants obtained from conductivity data at 18° are:-[96]

	m	α	K
$NaBrO_3$	0·05	0·991	3·6
	0·10	0·983	3·3

The heats of dilution at concentrations less than 0·1 N. at 25° are found to be in agreement with the activity coefficients.[97]

Sodium bromate crystallizes in the cubic system and X-ray investigation shows it to have space group T^4-$P2_13$; the unit cell contains four molecules. The sodium and bromine atoms are said to be displaced slightly from the positions they would occupy in the true NaCl-type structure. The atomic parameters have been measured by several investigators[98-103] and there is some disagreement in the values quoted:

TABLE VIII. - ATOMIC PARAMETERS OF SODIUM BROMATE

Reference	u_{Na}	v_{Br}	x	y	z
98	0·083	0·417	0·500	0·417	0·306
99	0·09	0·41	0·300	0·60	0·47
103	0·075	0·405	0·258	0·614	0·480

Interatomic distances Na-O = 2·38, Br-O = 1·78 and O-O = 2·95 A. with the bromine atom 0·53 A. above the plane of the oxygen atoms and the bond angle 111°48 are reported.[103] This Br-O distance is greater than those reported in much earlier investigations.[98,99]

Sodium chlorate and sodium bromate form a complete isomorphous series of cubic crystals, the cell dimensions varying from 6·559 A. for 100% $NaClO_3$ to 6·719 A. for 100% $NaBrO_3$.[104,113] Sodium and potassium bromates do not form solid solutions.

It has been suggested that there is a change in the lattice construction of sodium bromate crystals grown in a solution of a dye which is selectively adsorbed. In certain cases this results in a modification of the normal crystal habit and small variations in cell dimensions have also been noted.[105]

Sodium bromate crystallized in the presence of lead bromate or a lead salt may contain up to 0·01 mole-% of $Pb(BrO_3)_2$. This inclusion is apparently accompanied by a change of crystal habit.[113]

Cryoscopic measurements on sodium bromate solutions using a differential method have led to results in good agreement with the Debye-Hückel theory at low concentrations.[129]

Solubility and density determinations in the ternary systems:

$NaBrO_3$-$NaCl$-H_2O (at 10° and 25°),
$NaBrO_3$-$NaBr$-H_2O (at 10°, 25° and 45°),
$NaBrO_3$-NaI-H_2O (at 25°) and $NaBrO_3$-Na_2SO_4-H_2O (at 25°)

have given the following results:[108]

TABLE IX. - DETERMINATIONS OF SOLUBILITY AND DENSITY IN THE SYSTEMS $NaBrO_3$–$NaCl$–H_2O, $NaBrO_3$–$NaBr$–H_2O, $NaBrO_3$–NaI–H_2O and $NaBrO_3$–Na_2SO_4–H_2O.

$NaBrO_3$–$NaCl$–H_2O:-					
density of sat. soln. at 10°	1·211	1·192	1·213	1·229	1·235
NaCl g./100 g. soln.	0·00	9·84	20·75	23·61	24·52
$NaBrO_3$ g./100 g. soln.	23·24	12·75	6·41	5·32	5·02
density of sat. soln. at 25°	1·241	1·225	1·234	1·247	1·215
NaCl g./100 g. soln.	3·76	9·98	17·55	23·94	25·55
$NaBrO_3$ g./100 g. soln.	23·73	16·31	10·34	6·92	2·48
$NaBrO_3$–$NaBr$–H_2O:-					
density of sat. soln. at 10°	1·211	1·220	1·240	1·452	1·498
NaBr g./100 g. soln.	0·00	5·33	11·10	39·40	43·09
$NaBrO_3$ g./100 g. soln.	23·24	18·73	14·46	3·55	2·83
density of sat. soln. at 25°	1·257	1·270	1·282	1·377	1·542
NaBr g./100 g. soln.	0·00	6·46	13·82	29·83	39·24
$NaBrO_3$ g./100 g. soln.	28·29	22·38	16·72	7·86	4·61
density of sat. soln. at 45°			not given		
NaBr g./100 g. soln.	0·00	7·91	28·69	49·39	50·70
$NaBrO_3$ g./100g. soln.	34·22	26·55	11·17	3·72	3·50
$NaBrO_3$–NaI–H_2O:-					
density of sat. soln. at 25°	1·257	1·438	1·619	1·836	1·914
NaI g./100 g. soln.	0·00	32·21	48·11	60·65	64·00
$NaBrO_3$ g./100 g. soln.	28·29	8·92	3·62	1·44	1·17
$NaBrO_3$–Na_2SO_4–H_2O:-					
density of sat. soln. at 25°	1·284	1·303	1·317	1·254	1·205
Na_2SO_4 g./100 g soln.	4·09	12·35	16·45	19·17	21·90
$NaBrO_3$ g./100 g. soln.	24·96	18·71	15·85	7·06	0·00

The ternary systems $NaBr$–$NaBrO_3$–H_2O (at 35°), $NaBrO_3$–$NaHCO_3$–H_2O (at 25° and 35°), $NaBrO_3$–Na_2CO_3–H_2O (at 80°), $NaBrO_3$–$AgBrO_3$–H_2O (at 5°, 25° and 30°) and the quaternary systems $NaBr$–$NaBrO_3$–$NaHCO_3$–H_2O (at 25° and 35°) and $NaBr$–$NaBrO_3$–Na_2CO_3–H_2O (at 80°) have been investigated and the system $NaMoO_4$–$NaBrO_3$–H_2O (at 25°) has been considered in relation to the effect of reduction of molybdate by I^- and $S_2O_3^{--}$ on the determination of bromate in the presence of molybdate.[114,111,112]

The system $NaBrO_3$–Na_2SO_4–H_2O above 30° forms a single solid solution containing up to 18·5% of bromate (at 52°); this is thought to consitute a further type of solid solution not previously classified by Roozeboom.[109] In the system $NaBrO_3$–$NaClO_3$–H_2O (at 25° and 50°), the solubility curve appears to indicate the following solid phases:- (i) pure sodium bromate, (ii) a solid solution containing up to 5 - 10% sodium chlorate in sodium bromate, (iii) a solid solution containing from 0 to 65% of sodium bromate in sodium chlorate.[110]

From their study of the ternary system $NaBr$–$NaBrO_3$–H_2O, Klebanov and Basova suggest that sodium bromate is best prepared from solutions containing sodium bromide by evaporation to the point of crystallization followed by cooling to 10°; the systems

$NaBr$–$NaHCO_3$–H_2O, $NaBr$–Na_2CO_3–H_2O, $NaBrO_3$–$NaHCO_3$–H_2O,
$NaBrO_3$–Na_2CO_3–H_2O, $NaBr$–$NaBrO_3$–$NaHCO_3$–H_2O, $NaBr$–$NaBrO_3$–Na_2CO_3–H_2O

have also been studied and methods for obtaining the pure bromate from solutions containing bicarbonate or carbonate are suggested.[114]

With hydrogen in a silent electric discharge sodium bromate is reduced to sodium bromide;[106] magnesium amalgam has a similar effect.[107] Among many suggested uses for sodium bromate is that as an oxidizing agent in the permanent waving of human hair: the probable reactions which take place have been discussed.[115]

From measurements of the heat of dilution of dilute solutions of sodium bromate at 25° a value for the heat of formation in aqueous solution at infinite dilution, $Qf = 68{\cdot}68$ kg.-cal./mole, has been obtained.[197]

POTASSIUM BROMATE

The preparation of potassium bromate by the electrolysis of potassium bromide solutions using carbon electrodes has been investigated.[116] Untreated carbon electrodes were found to disintegrate rapidly; by filling the pores of the electrodes with paraffin, however, their life was extended considerably and the small quantity of carbon particles appearing in the solution after prolonged electrolysis could be filtered off easily. The efficiency of the cell, on the basis of bromate produced, using a depolarizer to raise the yield, was found to be higher than with platinum electrodes.

The solubility of potassium bromate in water between 5° and 50° has been measured;[108] the results are given in Table X.

TABLE X. - SOLUBILITY OF POTASSIUM BROMATE IN WATER, 5 - 50°

t°	5	10	15	20	25	30	35	40	45	50
density of sat. soln.	1·024	1·035	1·042	1·048	1·054	1·062	1·074	1·083	–	–
g./100 g. sat. soln.	3·642	4·510	5·397	6·460	7·533	8·785	10·13	11·58	13·08	14·69

The solubility of potassium bromate between 134° and 312° has also been measured and is as follows:[117]

TABLE XI. - SOLUBILITY OF POTASSIUM BROMATE IN WATER, 134 - 312°

t°	134	149	160	170	186	204	226	249	265	279	297	312
g./100 g. sat. soln.	43·6	48·4	51·1	54·1	59·9	64·2	70·6	72·6	77·2	81·1	83·1	86·4

Solubility and equilibrium data have been measured in the ternary systems:

$KBrO_3$-KBr-H_2O (between 0° and 80°),	$KBrO_3$-KI-H_2O (at 25°)
$KBrO_3$-KNO_3-H_2O (at 25°),	$KBrO_3$-K_2SO_4-H_2O (at 25°),

results being shown in Table XII[106,118] (see page 761). In none of these systems was there any evidence of double-salt formation.

In the system $KBrO_3$-$KClO_3$-H_2O, investigated at 25°, the two salts were found to form solid solutions containing up to 3% of potassium chlorate in potassium bromate and 5% of potassium bromate in potassium chlorate, the series of solid solutions being apparently discontinuous.[1] The solubility of potassium bromate in mixtures of water and deuterium oxide was measured at 25° and the ratio of the solubilities in D_2O and water, expressed in moles of potassium bromate per 55·51 moles of solvent, is found to be 0·895.[119] Potassium bromate is soluble in liquid ammonia to the extent of 0·002 g./100 g. solvent at 25°.[120] It is insoluble in ethylenediamine,[121] soluble in liquid sulphur dioxide[122] and appreciably soluble in phosphorus oxychloride.[123]

The effect of additions of lithium chloride on the solubility of potassium bromate in ethyl alcohol of dielectric constant 25·7 was studied over the

TABLE XII.- DETERMINATIONS OF SOLUBILITY AND DENSITY IN THE SYSTEMS $KBrO_3$-KBr-H_2O, $KBrO_3$-KI-H_2O, $KBrO_3$-KNO_3-H_2O and $KBrO_3$-K_2SO_4-H_2O

$KBrO_3$-KBr-H_2O:-					
density of sat. soln. at 25°	1·381	1·392	1·237	1·089	1·054
KBr g./100 g. soln.	40·62	40·00	26·05	7·82	0·00
$KBrO_3$ g./100 g. soln.	0·00	1·43	2·06	4·29	7·533
$KBrO_3$-KI-H_2O:-					
density of sat. soln. at 25°	1·054	1·182	1·402	1·707	1·718
KI g./100 g. soln.	0·00	18·85	38·99	58·14	59·76
$KBrO_3$ g./100g. soln.	7·533	2·96	1·63	0·99	0·00
$KBrO_3$-KNO_3-H_2O:-					
density of sat. soln. at 25°	1·074	1·148	1·193	1·225	1·193
KNO_3 g./100 g. soln.	5·05	16·98	23·17	27·01	27·71
$KBrO_3$ g./100 g. soln.	5·61	4·23	4·00	3·90	0·00
$KBrO_3$-K_2SO_4-H_2O:-					
density of sat. soln. at 25°	1·066	1·100	1·108	1·103	1·083
K_2SO_4 g./100 g. soln.	2·67	8·20	9·35	9·45	10·76
$KBrO_3$ g./100 g. soln.	6·08	4·27	4·00	3·40	0·00

concentration range 10^{-3} to 10^{-4} mole/litre. The results showed the activity coefficient to be given by $\log f = 3{\cdot}76\,\mu^{1/2}$ and to be unaffected by the radius of the ions or by the properties of the solvent other than the dielectric constant.[126]

The conductivity and dissociation constant of aqueous solutions of potassium bromate have been measured;[40,124,125] thus values reported for the equivalent conductivity are:

moles $KBrO_3$/l.	0·1477	0·0936	0·0491	0·01107	0·001051	0·000544
Λ	103·6	107·5	112·3	122·4	126·43	127·27

and the change with temperature in values of the equivalent conductivity at infinite dilution is illustrated by the following results:-

$t°$	0	18	25	100
Λ_∞	68·2	107·1	129·36	338·05
reference	124	124	125	124

The dissociation constant $K = 4$ was obtained from several experiments.[125]

Osmotic and activity coefficients, given in Table XIII, have been calculated from data on isotonic solutions:[95,127]

TABLE XIII.- OSMOTIC AND ACTIVITY COEFFICIENTS OF POTASSIUM BROMATE

Concentration moles $KBrO_3$/l.	0·1	0·15	0·2	0·3	0·4	0·5	0·5
Osmotic coefficient (ϕ)	0·910	0·8944	0·881	0·858	0·837	0·816	0·822
Activity coefficient (γ)	0·745	0·702	0·674	0·625	0·585	0·552	0·553
Reference	95	127	95	95	95	95	127

In solutions of potassium bromate at low concentrations crysocopic data, obtained by a differential method, were found to be in good agreement with the

Debye–Hückel theory.[129] The solubility product of potassium bromate has been measured in solutions of alcohol containing 6% water and the results obtained were plotted to show that log. solubility product versus $\mu^{1/2}$ (where μ is the ionic strength) is a linear function.[128]

The viscosity of solutions of potassium bromate (Table XIV) between 0·1 and 0·002 molar has been determined at 25° and is given[130] by:-

$$\eta_{\text{computed}} = 1 + 0{\cdot}0058\,c^{1/2} - 0{\cdot}0008\,c.$$

TABLE XIV. - VISCOSITY OF SOLUTIONS OF POTASSIUM BROMATE AT 25°

c	0·002	0·005	0·010	0·020	0·053	0·100
η observed	1·00026	1·00045	1·00059	1·00077	1·00125	1·00176
η computed	1·00026	1·00040	1·00057	1·00080	1·00129	1·00175

Accurate measurements of the densities of dilute aqueous solutions of potassium bromate have been used to determine the total volume change which occurs on solution. The contraction on dissolving one mole of potassium bromate in an infinite volume of water at 18° has been calculated from these data as 7·8 cc.[131,132]

The entropy of potassium bromate, calculated from heat capacity data, is 35·65 ± 0·1 g.-cal.deg.$^{-1}$mole^{-1}.[133] Using a value of 0·50 for the activity coefficient of potassium bromate in a saturated solution and data for the heat of solution obtained by Stackelberg, the entropy of the bromate ion in a molar solution is calculated as 37·4 ± 1·0 g.-cal.deg.$^{-1}$mole^{-1}. This is in poor agreement with the earlier value obtained from data for barium bromate;[171] but by recalculating these results, using a revised value for the entropy of the barium ion, a value of 38·7 g.-cal.deg.$^{-1}$mole.$^{-1}$ is obtained for a molar solution of bromate ions.

The molar magnetic susceptibility of solid potassium bromate is $-52{\cdot}6 \times 10^{-6}$ c.g.s. units.[35] Potassium bromate shows a definite piezoelectric effect.[83] Its dielectric constant has been measured and a value of 7·3 has been obtained.[134] High frequency measurements of the dielectric constant in dilute solutions (less than 0·0015 g. equiv./litre) gave a value of 60 for potassium bromate.[85]

Commercial potassium bromate has been found to exhibit a very slight triboluminescence, which is perhaps due to potassium chloride, potassium iodide, potassium chlorate and potassium iodate which have been found as impurities. If traces of these are added to pure potassium bromate, however, no luminescence results. The systems $KBrO_3$-$KClO_3$, $KBrO_3$-KIO_3 showed no effect and $KBrO_3$-KCl, $KBrO_3$-KI only a very slight effect.[135]

Morphologically, potassium bromate belongs to the trigonal system (pseudo-cubic, CsCl type) and *X*-ray studies show it to have space-group C^5_{3v}-$R3m$ with $Z = 1$, $r = 4{\cdot}403 \pm 0{\cdot}005$ A. and $\alpha = 86°0' \pm 5'$. The atomic parameters are $t = 0{\cdot}500 \pm 0{\cdot}015$, $u = 0{\cdot}58 \pm 0{\cdot}03$ and $v = 0{\cdot}125 \pm 0{\cdot}03$. The interatomic distances are quoted as K–O = 2·67 A. and 3·11 A.; Br–O = 1·68 A.[136,137] The systems $KBrO_3$-$NaBrO_3$ and $KBrO_3$-$KClO_3$, investigated by *X*-ray methods, were found not to form solid solutions.[104]

The reactions that occur when potassium bromate is melted with potassium iodide in molecular ratios 1:2 and 1:1 have been studied quantitatively. This reaction is slower than the analogous reaction with chlorate and the heat change is less.[138]

The reaction $2KBrO_3 + I_2 \rightleftharpoons 2KIO_3 + Br_2$ has been investigated and found to take place directly without the addition of catalysts and without the formation of free acid.[139] The further reaction $2KI + Br_2 \rightleftharpoons 2KBr + I_2$ takes place in the presence of potassium iodide. With the latter in excess over potassium bromate the quantity of free iodine remains unchanged; with excess of potassium bromate, free bromine is formed.[139] Excess of potassium bromate reacts with selenium monochloride to liberate halogen and produce selenium dioxide.[141]

Reactions between solid potassium bromate and various compounds and solid elements have been studied.[142,143] Potassium bromate was allowed to react with sulphur, selenium and tellurium in an atmosphere with a relative humidity below that corresponding to a saturated solution of the most hygroscopic component. The reaction is thought to be initiated by a minimum quantity of water adsorbed on the crystal surface; ions in this film are able to give rise to reaction by direct contact with crystals of the other reactant. A vigorous to violent reaction results at room temperature under these conditions, the order of activity being Se>S>Te. The reaction is thought to proceed by a mechanism such as:-

$$\text{(i)}\quad S + 2H_2O \rightarrow SO_2 + 2H_2$$

$$\text{(ii)}\quad 3H_2 + KBrO_3 \rightarrow KBr + 3H_2O$$

$$\text{(iii)}\quad 3SO_2 + KBrO_3 \rightarrow 3SO_3 + KBr$$

$$\text{(iv)}\quad 2KBr + 2SO_3 \rightarrow K_2SO_4 + Br_2 + SO_2.$$

The effects of the products of decomposition of bromic acid on sulphur were investigated and mixtures of sulphur with potassium bromate were treated with a drop of concentrated sulphuric acid, with sulphur dioxide, with disulphur dibromide and with bromine. An explosive reaction was obtained only in the presence of water, and not with addition of bromine. Disulphur dibromide reacted to give bromine and a sulphate. A further mechanism based on the formation of disulphur dibromide and its subsequent hydrolysis has been postulated;[144] this reaction liberates sufficient heat to raise the temperature of the mixture to a point where rapid reaction occurs. With sulphuric acid there was found to be a concentration limit below which combustion does not occur.[145]

The induction period in the interaction of potassium bromate and stannous chloride in aqueous solution decreases linearly with increase in temperature.[146]

The separation of cations from anions according to the reaction:

$$H^+A^- + K^+ + BrO_3^- \rightleftharpoons K^+A^- + H^+ + BrO_3^-,$$

where A^- is one equivalent of adsorber, using the Permutit ion-exchange adsorber 'Zeo-Karb' in 0·1 N. solution at a pH$\sim$4, resulted in the reduction of the bromate ion.[147]

In the electrodeless discharge potassium bromate has been found to give potassium hypobromite and potassium bromide together with some bromine.[148-150] The use of potassium bromate instead of nitrogen trichloride (Agene) for bleaching flour has been suggested as the danger of explosion in the latter case is high. The potassium bromate is premixed with starch to ensure proper mixing with the flour.[151]

RUBIDIUM AND CÆSIUM BROMATES

Rubidium and cæsium bromates have been prepared by adding the metal hydroxide, obtained by the action of barium hydroxide on the metal bisulphate, to a solution of bromic acid. This was prepared by the action of bromine on silver bromate in a large amount of water. Excess of bromine was removed by a current of air continued for 1–2 days. The bromates were obtained in small, but well defined, crystals with no water of crystallization.[152,153]

The melting points of the two bromates are: rubidium bromate, 430°; cæsium bromate, 420°. Their solubilities in water are:[153]

$t°$	25	30	35	40
$RbBrO_3$ g./100 g.H_2O	2·93	3·55	4·28	5·08
$CsBrO_3$ g./100 g.H_2O	3·66	4·53	5·32	–

Refs. p. 770

Investigated morphologically, both bromates appear to crystallize in the hexagonal system. Their refractive indices, determined by a comparative method, appear to lie between $\mu = 2{\cdot}144$ and $\mu = 2{\cdot}22$ but have not been determined absolutely.[153] A value of $-75{\cdot}1 \times 10^{-6}$ c.g.s. units has been obtained for the molar magnetic susceptibility of caesium bromate.[35]

COPPER AND SILVER BROMATES

The paramagnetic absorption of copper bromate, $Cu(BrO_3)_2,6H_2O$ at 78 megacycles/sec. and at 90° and 77°K. has been determined.[166] The static susceptibility was found to be 2·44 Bohr magnetons per ion and the spin relaxation time, $\zeta_0^1 = 7{\cdot}1 \times 10^{-9}$ sec. The paramagnetic dispersion of the salt was also investigated: no dispersion could be detected at 77°K. up to $\nu = 13{\cdot}2 \times 10^6$ Hz. and $H = 3200$ oersted.[167]

The solubility of silver bromate in the systems $AgBrO_3$–M_2SO_4 or MNO_3–H_2O (for K_2SO_4, $Mg(NO_3)_2$, $Ba(NO_3)_2$, Na_2SO_4, $CdSO_4$, $Ce(NO_3)_3$, KNO_3 and $MgSO_4$) has been recorded and the results are found to be approximately in accord with with the Lewis and Randall formula, $\alpha = f(\Sigma cv^2)$, where α is the activity of the ion and c and v are the molality and valence of each ion. Variations of up to 10% from the expected values were found.[154] Measurements of the solubility of silver bromate in the systems $AgBrO_3$–$M(NO_3)_2$–H_2O (M = Mg, Ca, Sr, Ba) have afforded the following results at 25°:-[155]

TABLE XV. - SOLUBILITY OF SILVER BROMATE (MOLAR × 10^2) IN AQUEOUS SOLUTIONS OF NITRATES

	$Mg(NO_3)_2$	$Ca(NO_3)_2$	$Sr(NO_3)_2$	$Ba(NO_3)_2$
0·3 M. soln.	1·27	1·33	1·43	1·49
1·0 M. soln.	1·73	1·81	1·84	–

Values obtained for the solubility of silver bromate in water at 25° show a wide variation; thus values of 0·00806 mole/l.,[155] 0·00813 mole/l.,[157] 0·00812 mole/l.,[156] 0·00827 mole/l.,[165] 0·00999 mole/l.,[154] 0·00995 mole/l.,[158] have been given for this quantity at various times. The system $AgBrO_3$–$NaBrO_3$–H_2O has been investigated at 5°, 25° and 30° and the salts are found to form a compound $AgBrO_3,NaBrO_3$ which forms a continuous range of solid solutions with silver bromate. Sodium bromate also forms a solid solution with silver bromate containing up to 2·5 - 3·0% of the latter. These results have been used to explain the variation in the reported values for the solubility of silver bromate.[111]

The solubility of silver bromate in binary mixtures of water with methyl alcohol, ethyl alcohol, *iso*propyl alcohol, *n*-propyl alcohol, acetone, ethylene glycol, glycerol, mannitol and glycine at 25° has been determined and the results, given in Table XVI, indicate that the Born equation is inadequate.[156,157]

TABLE XVI. - SOLUBILITY OF SILVER BROMATE IN MIXTURES OF ORGANIC SOLVENTS WITH WATER AT 25°

Wt.-% organic solvent	5	10	15	20	30	40	50	60	70
Methyl alcohol; d_{25} of solvent	–	0·9802	–	0·9650	0·9492	0·9318	0·9123	0·8908	–
Millimoles $AgBrO_3$ per litre sat. soln.	–	5·51	–	3·79	2·65	1·82	1·24	0·83	–

TABLE XVI. - SOLUBILITY OF SILVER BROMATE IN MIXTURES OF ORGANIC SOLVENTS WITH WATER AT 25° continued:

Wt.-% organic solvent	5	10	15	20	30	40	50	60	70
Ethyl Alcohol, d_{25}	–	0·9804	–	0·9664	0·9507	0·9315	0·9099	–	–
AgBrO$_3$ millimoles per l.	–	5·53	–	3·86	2·78	1·97	1·36	–	–
n-Propyl alcohol, d_{25}	–	0·9821	–	0·9674	0·9472	0·9261	0·9051	–	–
AgBrO$_3$ millimoles per l.	–	5·80	–	4·36	3·31	2·41	1·63	–	–
*iso*Propyl alcohol, d_{25}	no densities given								
AgBrO$_3$ millimoles per l.	–	5·50	–	3·95	2·92	2·10	1·50	–	–
Acetone, d_{25}	–	0·9845	–	0·9700	0·9537	0·9355	–	–	–
AgBrO$_3$ millimoles per l.	–	5·92	–	4·29	3·00	2·03	–	–	–
Mannitol, d_{25}	1·0147	1·0328	1·0513	–	–	–	–	–	–
AgBrO$_3$ millimoles per l.	8·24	8·38	8·51	–	–	–	–	–	–
Glycine, d_{25}	1·0184	1·0394	1·0613	–	–	–	–	–	–
AgBrO$_3$ millimoles per l.	12·9	18·4	24·9	–	–	–	–	–	–
Ethylene glycol, d_{25}	–	1·0097	–	1·0228	1·0362	1·0496	1·0624	–	1·0851
AgBrO$_3$ millimoles per l.	–	7·26	–	6·50	5·85	5·26	4·70	–	3·61
Glycerol, d_{25}	–	1·0207	–	1·0453	1·0706	1·0971	1·1239	1·1511	1·1784
AgBrO$_3$ millimoles per l.	–	7·80	–	7·49	7·15	6·84	6·48	6·08	5·59

The solubility of silver bromate in aqueous solutions of other organic solvents has also been measured[158] at 25° (see Table XVII, page 766).

The solubility of silver bromate in very dilute ammonia solutions has been used as evidence for the formation of a monammine-silver ion with an instability constant of $4{\cdot}3 \times 10^{-4}$.[159] Recalculation of previous data for the diammine-silver ion indicates a dissociation constant of $6{\cdot}2 \times 10^{-8}$.[159]

The values obtained for the solubility of silver bromate in aqueous pyridine solutions are :-[160]

Pyridine, mole/l.	0·00597	0·00827	0·01273	0·01564
AgBrO$_3$, mole/l. × 10^3	9·80	10·32	11·49	12·34

These results have been interpreted in terms of two complex ions, $\mathrm{Ag(C_5H_5N)^+}$ and $\mathrm{Ag(C_5H_5N)_2^+}$, for which the following dissociation constants are calculated:

$$K_1\ [\mathrm{Ag(C_5H_5N)^+}] = 1{\cdot}0 \times 10^{-2}$$

$$K_2\ [\mathrm{Ag(C_5H_5N)_2^+}] = 7{\cdot}8 \times 10^{-5}.$$

TABLE XVII. - SOLUBILITY OF SILVER BROMATE IN AQUEOUS SOLUTIONS OF ORGANIC SOLVENTS AT 25°

Allyl alcohol, mole/litre	0·585	0·293	0·146	0·0732
$AgBrO_3$ mole/l. × 10^2	2·98	2·20	1·69	1·38
Crotyl alcohol, mole/litre	0·702	0·527	0·351	0·0878
$AgBrO_3$ mole/l. × 10^2	1·87	1·73	1·54	1·16
Ethylvinylcarbinol, mole/l.	0·472	0·0944	0·0472	
$AgBrO_3$ mole/l. × 10^2	2·68	1·52	1·28	
Vinylacetic acid, mole/l.	0·467	0·117	0·0585	
$AgBrO_3$ mole/l. × 10^2	2·90	1·67	1·37	
Methylallyl alcohol, mole/l.	0·470	0·118	0·059	
$AgBrO_3$ mole/l. × 10^2	2·42	1·48	1·27	
Methylvinylcarbinol, mole/l.	0·255	0·102	0·025	
$AgBrO_3$ mole/l. × 10^2	2·12	1·53	1·14	
2-Methyl-2-buten-1-ol, mole/l.	0·100	0·020		
$AgBrO_3$ mole/l. × 10^2	1·21	1·05		
Phenol, mole/litre	0·448	0·112		
$AgBrO_3$ mole/l. × 10^2	1·28	1·07		

The effect of additions of silver nitrate, sodium nitrate and sodium benzenesulphonate on the solubility of silver bromate in an aqueous solution of *iso*propyl alcohol of dielectric constant 25·6 has been investigated and the results are in accordance with the equation, $\log f = 3{\cdot}76\,\mu^{1/2}$. The activity coefficient does not appear to be affected by any property of the solvent or of the ions other than the dielectric constant.[126]

By using a Cellophane membrane it has been possible to demonstrate the presence of colloidal particles in solutions of silver bromate in diethylamine.[161]

The entropy of silver bromate under standard conditions has been estimated as $S^{\circ}_{298} = 37{\cdot}3 \pm 0{\cdot}6$ g.-cal.deg^{-1}mole^{-1}.[91] The compressibility has been measured over the range 0–100,000 kg./sq.cm. and the volume decrement, $\Delta v/v_0$ is found to be 0·104 for the range 0–50,000 kg./sq.cm., and 0·05 for the range 50,000–100,000 kg./sq.cm.[94,162]

Silver bromate has the perovskite type structure and the unit cell dimensions are reported as a = 8·59, c = 8·01 A.[163] This space group is D_{4h}^{17}-*I4/mmm* and there are eight molecules in the unit cell.

The reaction $AgBrO_3 + I_2 \rightleftharpoons AgIO_3 + Br_2$ has been investigated and is found to proceed quantitatively to the right in 10 minutes at 22°.[164]

Variations of the e.m.f. of silver bromate electrodes have been investigated and are said to be due to the formation of metastable hair-like crystals of silver bromate. These are reported to have a higher solubility than the stable tetragonal form and to be stable at about 100°.[165]

The reactions of silver bromate with sulphur, selenium and tellurium are similar to those of potassium bromate.[143,144]

ALKALINE EARTH BROMATES

The magnetic susceptibilities of the alkaline earth bromates have been measured[35] and are shown in Table XVIII, page 767.

The anhydrous oxides of the alkaline earth metals form addition compounds of the type $MOBr_2$ with bromine; those derived from strontium oxide and barium oxide decompose under the action of excess of bromine with the formation of bromate and loss of oxygen.[168]

TABLE XVIII. - MAGNETIC SUSCEPTIBILITY OF ALKALINE EARTH BROMATES

	$Ca(BrO_3)_2$	$Ca(BrO_3)_2,H_2O$	$Sr(BrO_3)_2$	$Ba(BrO_3)_2$	$Ba(BrO_3)_2,H_2O$
Susceptibility c.g.s. units 10^{-6}	-84·9*	-97·3	-93·5	-105·8	-117·5

* (−84·5 × 10^{-6} measured in solution)

Barium bromate has been prepared, in a yield of 410 g., by treating a hot solution of 345·7 g. of potassium bromate in 700 cc. of water with a hot solution of 253 g. of barium chloride ($BaCl_2,2H_2O$) in 400 cc. of water. The mixture is allowed to cool and the liquid decanted to leave crystals of barium bromate which should be washed with cold water.[169]

The dissociation constant of barium bromate has been determined from conductivity data at 18°;[96] in Table XIX m is the concentration of the aqueous solution in g.-mol./l., α is the fraction of bivalent radical existing in the form of intermediate ion according to the scheme $BU_2 \rightarrow BU + U$; $BU \rightleftharpoons B + U$, and log K is calculated from the Debye-Hückel equation:-

TABLE XIX. - DISSOCIATION CONSTANT OF BARIUM BROMATE

m	α	$\log K$
0·0025	0·028	−0·931
0·005	0·040	−0·855
0·010	0·065	−0·864
0·020	0·095	−0·856

The solubility of barium bromate in aqueous potassium chloride and glycine solutions at 25° has been measured:-[170]

TABLE XX. - SOLUBILITY OF BARIUM BROMATE IN AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE AND OF GLYCINE AT 25°

KCl mole/litre	0·000	0·02008	0·04019	0·06034	0·08050	0·1007
$Ba(BrO_3)_2$ mole/l. × 10^2	2·008	2·135	2·233	2·330	2·416	2·483
Glycine mole/l.	0·0251	0·0503	0·0755	0·1008		
$Ba(BrO_3)_2$ mole/l. × 10^2	2·045	2·081	2·113	2·150		

The specific heat of barium bromate monohydrate was measured from 16° to 300°K.; this together with the heat of solution and free energy of solution was used to calculate the entropy of barium bromate;[171] a value of S°_{298} = 80·72 g.-cal.deg.$^{-1}$mole^{-1} was obtained. The original results gave S°_{298} = 43·6 g.-cal. deg.$^{-1}$ mole^{-1} for the bromate ion, but a recalculation using a revised value for the entropy of the barium ion gave a value of S°_{298} = 38·7 g.-cal.deg.$^{-1}$mole^{-1} which is in better agreement with that obtained from studies on potassium bromate.[133] The heat of solution of crystalline barium bromate monohydrate has been measured and values of −15·06 kg.-cal. and 235·0 kg.-cal. are obtained for the heat of solution and heat of formation respectively [171]

The crystalloluminescence of barium bromate is most noticeable during the slow crystallization of a saturated solution over the range 72° to 55°.[172,173] No activating impurities are found to be required.

MAGNESIUM, ZINC, CADMIUM AND MERCURY BROMATES

Zinc bromate hexahydrate crystallizes in the cubic system. The space group is $T_h^6 - Pa^3$ and the unit cell contains four molecules; a = 10·31 A. The structure consists of octahedral $Zn.6H_2O$ groups arranged on the triad-axes and pyramidal BrO_3 groups. Parameters quoted are:-[174,175]

Br: 0·259, 0·259, 0·259
H_2O: 0·195, 0·050, 0·965
O: 0·140, 0·145, 0·330
Zn: at face-centred positions.

The anodic oxidation of mercuric bromide with a platinum anode was found to liberate bromine at the anode and mercuric bromate was formed until all the mercuric bromide had been consumed. With the electrodes out of contact with the mercuric bromide neither bromine nor bromate was formed. The reactions involved are thought to be: (1) oxidation of mercuric bromide to mercuric bromate and (2) the formation of a little bromic acid and a large quantity of hydrobromic acid which react to liberate bromine.[176]

Mercuric bromate dihydrate has been prepared by adding the equivalent amount of mercuric perchlorate to a hot 3 N. solution of perchloric acid nearly saturated with sodium bromate. The solution is then cooled to 0° and the crystals are washed with water and centrifugally drained (yield 85%). The anhydrous salt can be obtained by dehydrating over calcium chloride at room temperature. The basic salt, $Hg(OH)BrO_3$, has been made by a similar method using proportions indicated by the equation,

$$Hg(ClO_4)_2 + NaBrO_3 + H_2O = Hg(OH)BrO_3 + NaClO_4 + HClO_4$$

a slight excess of sodium bromate should be used and the basic salt dried at 130 - 140°. The solubilities of the normal and basic salts at 25° in aqueous solutions of perchloric and nitric acids are given in Table XXI:-[177]

TABLE XXI. - SOLUBILITY OF NORMAL AND BASIC MERCURIC BROMATE IN AQUEOUS PERCHLORIC AND NITRIC ACIDS AT 25°

Approximate normality	1·0	2·0	3·0	4·0	5·0
$HClO_4$: $Hg(BrO_3)_2$ g./100 cc. sat. soln.	–	6·58	4·13	2·58	1·5
basic salt g./100 cc. sat. soln.	4·34	5·94	6·06	–	–
HNO_3: $Hg(BrO_3)_2$ g./100 cc. sat. soln.	–	14·66	15·00	14·99	14·75
basic salt g./100 cc. sat. soln.	12·52	21·30	–	–	–

The solubility of mercuric bromate in water at 25° is 0·081 g./100 cc. saturated solution.

RARE EARTH BROMATES AND GALLIUM, INDIUM AND THALLIUM BROMATES

The solubilities in water of the hydrated bromates of lanthanum, praseodymium, neodymium, samarium, gadolinium and terbium of the type $M(BrO_3)_3,9H_2O$ have been measured.[178] The order of solubility has also been investigated by fractional crystallisation at 20 - 25° and is found to be Er>La>Yt>Ho>Pr>Nd>Tb>Gd.[179] (See Table XXII, page 769).

Neodymium bromate, $Nd(BrO_3)_3,9H_2O$, has space group C^4_{6v}-C_6mc: there are two molecules per unit cell which has a = 11·73 c = 6·76 A. The Nd^{3+} ion is surrounded by nine water molecules in regular fourteen-sided polyhedra consisting of trigonal prisms with raised prism face-centres. The neodymium ions occupy the positions ⅓, ⅔, ¼ and ⅔, ⅓, ¾ thus forming strings of these polyhedra parallel to the c-axis. The bromate ions are situated in strings along the line $x = y = 0$. Nd-H_2O distances are 2·50 ± 0·05 A.; H - bond distances between water and oxygen in the bromate ions are 2·77 ± 0·10 A., Br-O distances 1·74 ± 0·07 A.[180]

Gadolinium bromate, $Gd(BrO_3)_3,9H_2O$, has been described as melting at 80°; it decomposes at 85°. Crystallographically, it is hexagonal-bipyramidal with $a{:}c = 1{:}0{\cdot}5690$.[181-183]

TABLE XXII. - SOLUBILITIES OF HYDRATED RARE EARTH METAL BROMATES IN WATER

t°	0	5	10	15	20	25	30	35	45
$La(BrO_3)_3,9H_2O$ g./100 g. water	184·5	214·7	251·3	298·4	363·0	462·1	688·6	1061·5	–
$Pr(BrO_3)_3,9H_2O$ g./100 g. water	88·55	105·86	123·46	144·1	167·9	196·1	235·5	278·5	434·5
$Nd(BrO_3)_3,9H_2O$ g./100 g. water	66·35	80·06	94·57	111·32	128·6	151·3	175·9	205·8	289·9
$Sm(BrO_3)_3,9H_2O$ g./100 g. water	49·78	60·21	72·47	85·91	100·6	117·3	135·5	157·2	214·1
$Gd(BrO_3)_3,9H_2O$ g./100 g. water	50·18	60·01	70·11	82·64	95·58	110·5	126·1	144·5	195·6
$Tb(BrO_3)_3,9H_2O$ g./100 g. water	66·42	77·34	89·68	102·4	117·1	133·2	151·9	172·9	227·1

Europium bromate, $Eu(BrO_3)_3,9H_2O$, has been investigated crystallographically and is hexagonal-bipyramidal with $a:c$ = 1:0·5714.[183] A basic holmium bromate, $Ho(BrO_3)_3,4Ho_2O_3$, has been prepared by dissolving the oxide in a hot concentrated solution of the bromate.[184]

The formation of gallium bromate in solution, by adding a solution of gallium sulphate to barium bromate until all the barium is precipitated as sulphate, has been reported. The solution obtained was weak owing to the low solubility of barium bromate and decomposed on being concentrated by heat.

The entropy of thallous bromate has been estimated as S°_{298} = 42·3 ± 1·5 g.-cal.deg.$^{-1}$mole^{-1}.[91] Thallous bromate is thought to have the same structure as potassium bromate, with space-group C_{3v}^5–$R3m$, cell constants a = 4·45, α = 87°24′ and the parameters: Tl at (0,0,0), Br at (u,u,u) and O at (u,v,w), where u = 0·492, v = 0·568, w = 0·126.[187]

LEAD, COBALT AND NICKEL BROMATES

The solubility of lead bromate at 25° is reported as 0·03437 mole/l. and the density of the saturated solution as 1·0112. The solubility has also been determined in aqueous solutions of various concentrations containing the nitrates of potassium, sodium, lithium, calcium, strontium and lead:-[188]

TABLE XXIII. - SOLUBILITY OF LEAD BROMATE IN AQUEOUS SOLUTIONS OF NITRATES AT 25°

KNO_3 mole/l.	0·00	0·09934	0·2950	0·5784	1·1850	2·6423
d_{25} sat. soln.	1·0112	1·0181	1·0378	1·0608	1·1127	1·2220
$Pb(BrO_3)_2$ mole/l.	0·03437	0·04373	0·05798	0·07577	0·1134	0·1732
$NaNO_3$ mole/l.	0·04833	0·3938	0·9655	1·4241	2·6860	7·1770
d_{25}	1·0141	1·0424	1·0837	1·1158	1·2010	1·4824
$Pb(BrO_3)_2$ mole/l.	0·03884	0·06144	0·08899	0·1098	0·1651	0·3416
$LiNO_3$ mole/l.	0·04925	0·3012	0·5815	1·4259	2·7213	4·9703
d_{25}	1·0135	1·0293	1·0446	1·0880	1·1507	1·2562
$Pb(BrO_3)_2$ mole/l.	0·03849	0·05365	0·06517	0·09337	0·1310	0·1930
$Sr(NO_3)_2$ mole/l.	0·005566	0·05020	0·3903	0·7614	1·7789	2·8704
d_{25}	1·0117	1·0226	1·0933	1·1627	1·3438	1·5261
$Pb(BrO_3)_2$ mole/l.	0·03581	0·04455	0·08177	0·1110	0·1765	0·2228

TABLE XXIII. - SOLUBILITY OF LEAD BROMATE IN AQUEOUS SOLUTIONS OF NITRATES AT 25° continued:

$Ca(NO_3)_2$ mole/l.	0·006271	0·05162	0·3352	0·7780	1·7872	3·1950
d_{25}	1·0099	1·0195	1·0643	1·1283	1·2607	1·4215
$Pb(BrO_3)_2$ mole/l.	0·03565	0·04298	0·07497	0·1105	0·1649	0·2118
$Pb(NO_3)_2$ mole/l.	0·004947	0·04981	0·2955	0·4871	0·7672	1·3807
d_{25}	1·0104	1·0219	1·0936	1·1480	1·2290	1·4011
$Pb(BrO_3)_2$ mole/l.	0·03371	0·03161	0·03457	0·03876	0·04572	0·06183

The formation of solid solutions of lead and sodium bromates has been investigated and the effect of included lead bromate on the crystal growth of sodium bromate has been noted.[113]

Following a serious explosion, which caused two deaths and considerable damage, in a German industrial laboratory during the preparation of lead bromate from potassium bromate and excess of lead acetate, the dangers of this method of preparation have been discussed at length.[189-193] The explosive entity formed during the process is thought to be a complex acetate and bromate of lead which explodes at 165° or by percussion at room temperature.

The crystal structures of cobalt bromate hexahydrate, $Co(BrO_3)_2,6H_2O$, and nickel bromate hexahydrate, $Ni(BrO_3)_2,6H_2O$ have been investigated. They are found to be isomorphous, cubic, with space-group T_h^6-Pa3. The unit cell contains four molecules. The measured densities are 2·55 g./c.c. for the cobalt salt and 2·60 g./c.c. for the nickel salt; the unit cell sides are a = 10·32 ± 0·005 A. and 10·272 ± 0·002 A. respectively.[194]

PERBROMIC ACID AND PERBROMATES

Attempts to isolate perbromic acid or perbromates or to prove their presence have so far been unsuccessful,[195] and the reasons for the non-existence of perbromic acid and perbromates have been discussed.[196]

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SECTION XXVII

THE SPECTROSCOPY OF BROMINE, IODINE MONOBROMIDE, HYDROGEN BROMIDE AND BROMINE OXIDES

By R. F. BARROW

THE BROMINE ATOM: OPTICAL SPECTRA

A classified list of the more important work on the optical spectra of the bromine atom is given in Table I. Many of these spectra are as yet known only very incompletely.

TABLE I.- INVESTIGATIONS OF THE OPTICAL SPECTRA OF THE BROMINE ATOM

Reference	Spectrum	λλ, A.	Notes
1	I,II	4014 - 5332	Zeeman effect
2	I	1232 - 1634	-
3	I,II	-	Zeeman effect
4	I,II	-	-
5	I,II	2270 - 6560	Pressure and Stark effects
6	I,II	3794 - 4800	Stark effect: qualitative
7	I - III	2000 - 6000	-
8,9	I - III	2250 - 6750	-
10	I	2240 - 3150	-
11	I	3735 - 9320	-
12	I,II	650 - 2300	Zeeman effect
13	II	1300 - 2250	-
14	II - V	2300 - 6225	-
15	II	4700 - 4900	Zeeman effect
16	II	-	-
17	II	-	-
18	II	4477 - 5183	Interferometric wave-lengths
19	II	-	-
20	II	-	-
21	III	-	-
22	III	{ 665 - 818 2234 - 4520	-
23	IV	{ 538 - 736 2179 - 3042	-
24	V - VII	480 - 860	-
25	VIII	138, 139	-

This work is summarized in the tables of Moore,[26] which also include the results of unpublished work by Kiess and by Edlén. Term-values for the lowest electronic states of the bromine atom, and values of the ionization potentials are given in Table II.

The hyperfine structure of lines in the spectra of Br I and Br II has also been investigated.[27-34] Deviations from the interval rule have been used to

TABLE II. - TERM VALUES AND IONIZATION POTENTIALS FOR THE BROMINE ATOM[26]

Term-values, cm.$^{-1}$			Ionization potentials, eV.			
$4s^2.4p^4.5s$	$^2P_{1/2}$	68 963·52	Br I	11·84	$4p^5$	$^2P_{3/2}$
	$^2P_{3/2}$	67 176·87	II	21·6	$4p^4$	$^3P_2$
	$^4P_{1/2}$	66 877·16	III	35·9	$4p^3$	$^4S_{3/2}$
	$^4P_{3/2}$	64 900·50	IV	-	$4p^2$	$^3P_0$
	$^4P_{5/2}$	63 429·82	V	-	$4p$	$^2P_{1/2}$
$4s^2.4p^5$	$^2P_{1/2}$	3 685	VI	-	$4s^2$	$^1S_0$
	$^2P_{3/2}$	0	VII	-	$4s$	$^2S_{1/2}$
			VIII	193	$3d^{10}$	$^1S_0$

determine approximate values of the nuclear quadrupole moment and of the nuclear magnetic moment.[33] Reviews of hyperfine structure observations[35] and of nuclear properties[36,37] have been given: values[38] of the latter are as follows:-

	Mass (a.m.u.)	Spin	Magnetic moment (n.m.)	Quadrupole moment (10^{-24} cm^2.)
^{79}Br	78·94438	3/2	2·10576	+0·335
^{81}Br	80·94228	3/2	2·2696	+0·280

Values of the nuclear quadrupole moments, Q, have also been obtained from the coupling constants, eQq, obtained from observations of the fine-structure in the micro-wave region. For example, observations[39] on cyanogen bromide have given the values $Q(^{79}\text{Br}) = +0{\cdot}28 \times 10^{-24}$, $Q(^{81}\text{Br}) = +0{\cdot}23 \times 10^{-24}$ cm^2. However the evaluation of Q in this way from values of eQq depends upon the assumptions[38] made in estimating q ($= \partial^2V/\partial z^2$), and Gordy[40] obtained +0·31 and +0·26 × 10^{-24} cm^2. for ^{79}Br and ^{81}Br respectively. These values are superseded by those given in the table above, which were determined by atomic beam experiments.[49]

The excitation of bromine lines for analytical purposes has been considered[41,42] (see also [10], and page 808). An atlas giving spectra of Br I and Br II has been published.[43] According to the M.I.T. list[44] the following are the strongest lines in the wave-length region between 2000 and 10000 A.:-

Wave-length, A.	Excitation potential, volts.
4816·71	14·4
4785·50	14·4
4704·86	14·4

These lines arise from Br$^+$. The spectrum of a spark discharge in liquid bromine is found to be continuous,[47] with a short wave-length edge at 6000 A.

Wave-functions for the ion Br$^-$, and for the neutral atom have been computed;[45] for a review, see Hartree.[46] Calculations of Russell-Saunders intervals in Br III have been made.[48]

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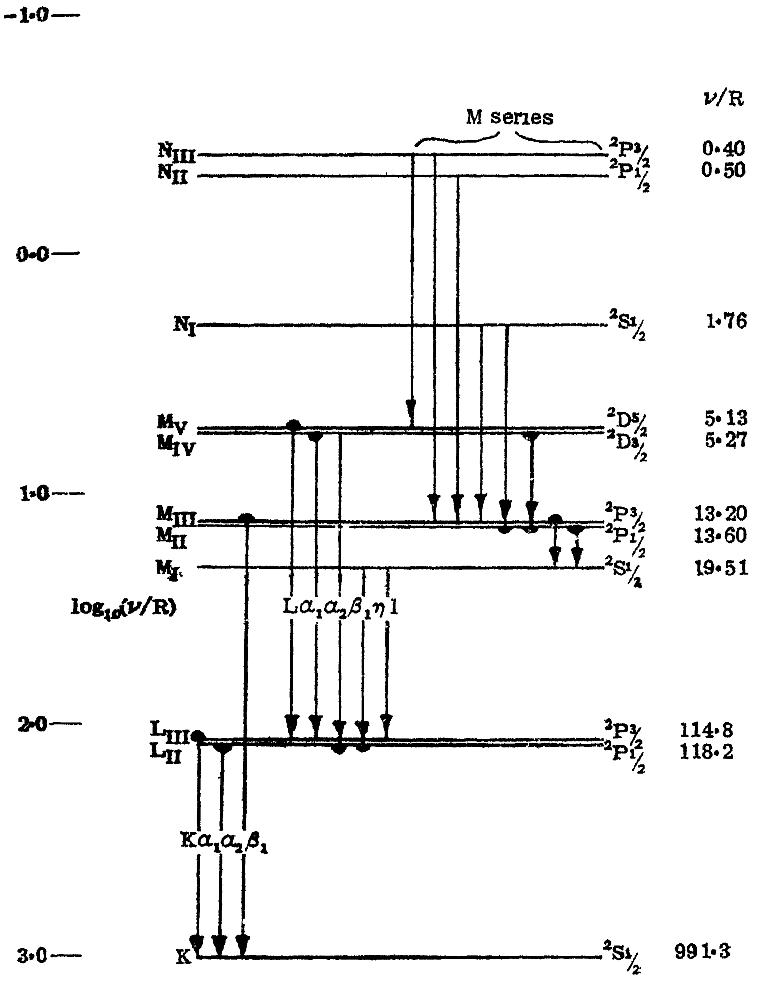
X-RAY SPECTRA

A number of measurements of wave-lengths in the *K*-series,[1-7] *L*-series[8-11] and *M*-series[12] in emission have been made. As a result, quite precise values for the *X*-ray energy levels in the bromine atom are available (see Fig. 1). Theoretical considerations relating to these levels are discussed.[13,14,38]

The *K*-absorption edge of bromine[15,16] shows in many cases a structure[17-26] which varies with the nature of the absorbing substance. For example, the details of the *K*-absorption spectrum are different for bromides and bromates,[17,18,22] and gaseous bromine shows a pronounced structure near the short-wave-length side of the absorption limit,[23,24] which does not appear in liquid or solid bromine[23] or in gaseous hydrogen bromide.[23,24] The theoretical interpretation of the absorption spectrum in gaseous bromine and hydrogen bromide has been discussed.[25] The essential point is that of the scattering of the ejected photo-electron by the partner atoms in the molecule.[19] The direct and scattered electron waves interfere to increase or decrease the chance of ejection of a photo-electron according to whether the interference is constructive or destructive. Now the probability of


-1·0
0·0
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log$_{10}$(ν/R)
M series
ν/R
N$_{III}$
N$_{II}$
N$_I$
M$_V$
M$_{IV}$
M$_{III}$
M$_{II}$
M$_I$
L$_{III}$
L$_{II}$
K
$^2P_{3/2}$ 0·40
$^2P_{1/2}$ 0·50
$^2S_{1/2}$ 1·76
$^2D_{5/2}$ 5·13
$^2D_{3/2}$ 5·27
$^2P_{3/2}$ 13·20
$^2P_{1/2}$ 13·60
$^2S_{1/2}$ 19·51
$L\alpha_1\alpha_2\beta_1\eta l$
$^2P_{3/2}$ 114·8
$^2P_{1/2}$ 118·2
$K\alpha_1\alpha_2\beta_1$
$^2S_{1/2}$ 991·3

Fig. 1. X-RAY ENERGY LEVELS IN BROMINE, ON A LOGARITHMIC SCALE. (THE POSITION OF L$_I$ IS NOT KNOWN). ARROWS ILLUSTRATE SOME OF THE OBSERVED TRANSITIONS.

ejection of a photo-electron is the same as that of the absorption of an *X*-ray. Thus the interference may lead to a rise or fall in the absorption coefficient from the value that would be found in the absence of the partner atoms in the molecule (see also page 625). Contrary to Wilhelmy,[27] the $K\alpha_1$ line of bromine is not observably affected either by chemical combination or by physical state of aggregation.[28]

The absorption of bromine in the region of the *L*-discontinuities does not appear to have been studied: the $M_{IV,V}$ head has been observed.[29]

Clark and Duane[30] observed the *K*-spectrum of bromine in reflection from crystals of $CsIBr_2$ following irradiation with continuous *X*-rays: the reflections from potassium bromide crystals have been studied in a similar way.[31] The magnetic spectrum of electrons ejected from bromine by molybdenum *K*-radiation has been examined.[32] Measurements have been made of the fluorescence yield[33] – the ratio of the number of fluorescent *K*-quanta to the number of photo-electrons ejected from the *K* shell. The relative intensities of lines in the *K*-series has been determined.[34,35] The mass absorption coefficient of bromine has been measured[36] at several wave-lengths between 0·16 and 1·93 A.; an empirical method of calculating these absorption coefficients has been given.[37]

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THE BROMINE MOLECULE, Br_2

Bromine vapour absorbs light throughout the spectrum from about 1500 A., the lower limit of the present investigations, to beyond 8000 A. In the green region, there is a characteristic set of bands, in which the separation between successive bands decreases with decreasing wave-length: a convergence limit is observed at about 5110 A., beyond which the absorption becomes continuous.[1-3] Franck[4] identified the energy corresponding to onset of the continuum with that required for the dissociation of the molecule into atoms, $Br(^2P_{3/2}) + Br(^2P_{1/2})$. The determination of the dissociation energy was subsequently considered,[5] and new measurements, leading to a more accurate value of the dissociation energy, have been made.[6,7]

However the early vibrational analyses[7,8] proved to be not quite correct.[9]

Further measurements were made,[10] but the accepted analyses rest on the work of Brown[11] and of Darbyshire.[12] Brown showed that there are two band-systems, which partly overlap. The correct vibrational analysis of the shorter wave-length system (5110 to 8675 A.) was settled by observation of the vibrational isotope effect. The strongest bands arise from the molecule $^{79}Br^{81}Br$, which is about twice as abundant as either symmetrical molecule. Brown[13] subsequently carried out a rotational analysis of a number of bands of this system, and showed that each band of a given molecular species contained a single *P* and single *R* branch, supporting the identification of the system as B $^3\Pi_{0+}$ - X $^1\Sigma^+$, as had already been postulated.[14] The branches assigned to $^{79}Br_2$ and $^{81}Br_2$ show alternating intensity, favouring values of the nuclear spin, $i = 3/2$, for both isotopes. It appears that the levels $v^1 = 3$ and 4 in B $^3\Pi_{0+}$ are perturbed by interaction with a neighbouring state.

The weaker system is A $^3\Pi_1$ - X $^1\Sigma^+$, and Brown[11] showed that the convergence limit in A $^3\Pi_1$ corresponds to dissociation into two bromine atoms in their ground states, $^2P_{3/2}$. Darbyshire[12] extended the analysis of this system (6450 to 8180 A.) and corrected the vibrational analysis by means of observations of the isotope effect.

Constants for these states are collected in Table III.

TABLE III. - CONSTANTS FOR THE $^{79}Br^{81}Br$ MOLECULE: STATES X A AND B

State	T_0	ω_e	$x_e\omega_e$	$y_e\omega_e$	Notes
B $^3\Pi_{0+u}$	15840	$165{\cdot}4$	$1{\cdot}577$	$-0{\cdot}0087$	1
A $^3\Pi_{1u}$	13737	$170{\cdot}7$	$3{\cdot}69$	-	1
X $^1\Sigma_g^+$	0	$323{\cdot}2$	$1{\cdot}07$	-	2
		$324{\cdot}2_6$	$1{\cdot}14_5$		3
		$323{\cdot}8_1$	$1{\cdot}15$		4
State	B_e	α_e	D_e	r_e, A.	
B $^3\Pi_{0+u}$	$0{\cdot}0595$	$0{\cdot}000625$	$2{\cdot}9 \times 10^{-8}$	$2{\cdot}66_3$	-
X $^1\Sigma_g^+$	$0{\cdot}0809_1$	$0{\cdot}000275$	$2{\cdot}0 \times 10^{-8}$	$2{\cdot}283_6$	5

Notes:

(1) The values of T_0 are somewhat uncertain: in state B there is some (small) error arising from an extrapolation, while in A, there is the possibility of error in the values of v'.
The values for the vibrational constants are valid only over a limited range of v'. Those for state A are taken from Darbyshire;[12] those for B from Rees.[15]

(2) From band origins.[13]

(3) From band-heads.[12]

(4) From resonance fluorescence.[16]

(5) The value of r'' obtained by electron diffraction[17] is $2{\cdot}279$ A.

(6) The convergence limit in B $^3\Pi_{0+u}$ is at 19585 cm.$^{-1}$, to Br ($^2P_{3/2}$) + Br ($^2P_{1/2}$). Thus $D_0'' = 15900$ cm.$^{-1}$, or $45{\cdot}45$ kg.-cal./mole. State A $^3\Pi_{1u}$ dissociates to give ground-state atoms.

If a gas, subject to a magnetic field, is examined between crossed nicols some light may be transmitted by the second nicol owing to a small rotation of the plane of polarization by the field (Faraday effect) and the resulting spectrum is known as the magnetic rotation spectrum. Since a rotation of the plane of polarization is large only in the immediate neighbourhood of absorption lines for which there are appreciable Zeeman effects, only part of each band appears in the magnetic rotation spectrum, which is therefore a more or less simplified version of the ordinary absorption spectrum. Such a spectrum has been observed for bromine.[32] The B - X system bands show a large number of closely spaced lines, the relative intensities of which do not change appreciably with the strength of the field, (see also [33,34]).

Details of the continua observed in absorption in gaseous bromine are given in Table IV and considered in more detail below. In hot bromine gas, at 950 to 1000°C., there appears a further very weak continuum with λ_{max} = 2930 A., which was observed[35] at 270 mm. pressure with a path-length of 150 cm.

TABLE IV.- CONTINUOUS ABSORPTION SYSTEMS OF GASEOUS BROMINE

Continuum	Transition	ν_{max}	ϵ_{max}	Reference
D	V, $^1\Sigma_u^+ \leftarrow$ N	(64000)	?> 10^3	18,19
C	? $\leftarrow$ N	44500	3·5	20,21
A	Q $^1\Pi_u \leftarrow$ N	24300	155	21,22
B	Q{ B $^3\Pi_{0^+} \leftarrow$ N A $^3\Pi_1 \leftarrow$ N	20740 (18630)	}70	21,22

Notes:-

(1) No quantitative measurements on continuum D have been made.

(2) Alternative interpretations of continua *A* and *B* have been put forward:[21] that given here now seems most probable.[22] According to this interpretation, most of the intensity of the *A* continuum is in the transition B $^3\Pi_{0^+} \leftarrow$ N.

(3) N is written for the ground state, X $^1\Sigma_g^+$.

Bands of the system B-X appear in emission[23] when bromine vapour is heated above about 450°C., when bromine burns in hydrogen,[24,25] or in oxy-methyl bromide or oxy-ethyl bromide flames.[26,27] In the thermoluminescence spectrum, there also appears a continuum extending to wave-lengths below 5100 A. which probably arises from the recombination[28,29] $Br + Br^* = Br_2 + h\nu$. The bands are also observed in discharge tubes.[36]

Although an attempt[37] to obtain an ultra-violet fluorescence failed, radiation of wave-length between 5000 and 5600 A. excites a green fluorescence[30] spectrum in bromine vapour. Plumley[16] used the mercury line 5461 A. and discovered five series of resonance doublets, which he was able to identify unequivocally. In the main series, the initial act of absorption is the transition from $J'' = 8$ in $v'' = 0$ of the ground state of $^{79}Br^{81}Br$ to $J' = 9$, $v' = 19$ in B $^3\Pi_{0^+}$. The doublet series then consists of the transitions ($J' = 9$, $v' = 19$) to $J'' = 10$ or $J'' = 8$ with successive values of v''. This series was followed as far as $v'' = 17$. Details of the series are given below:-

Series	Initial Transition	Species		ν	
I	19,0 *R*(8)	79,81	*F*(p)	-	+(- 3·0)
II	23,1 *R*(17)	81,81	*F*(p)	+4·3 *p*	+(- 6·0)
III	25,1 *P*(64)	79,81	*F*(p)	+3·35*p*	+(+20·5)
IV	21,0 *P*(74)	79,79	*F*(p)	-0·4 *p*	+(+24·0)
V	21,0 *R*(76)	79,81	*F*(p)	+1·65*p*	+(-25·0)

Here, $F(p) = 18307{\cdot}5 - 322{\cdot}67\,p + 1{\cdot}15\,p^2$, corresponding to
$\nu = 18469{\cdot}22 - 323{\cdot}81\,(v'' + \tfrac{1}{2}) + 1{\cdot}15\,(v'' + \tfrac{1}{2})^2$.

The doublet intervals in parentheses are to be omitted for the main lines and to be included to give the wave-numbers of the companions.

Plumley found that the intensity of this spectrum is about one three hundredth of that of the iodine fluorescence, and, in accordance with this trend, was unable to detect any fluorescence in chlorine. The intensity of fluorescence is rather insensitive to the pressure: thus at 6100 A., the intensity is about the same at 0·1 mm. as it is at 100 mm. pressure.

What was described as a Raman spectrum[31] of gaseous bromine was obtained by illuminating bromine at 900 mm. pressure with He 5875·6 A. Shifts were observed at 316·8, 631·3 and 944·5 cm.$^{-1}$ in a fifteen-hour exposure. Although it is indeed possible that the fundamental might be photographed in this time, the intensities of the overtones are likely to be several orders of magnitude smaller. Moreover, the values of the shifts obtained fit poorly with those calculated from the vibrational constants (Table III) on the assumption that the shifts are equal to $G''(1) - G''(0)$, $G''(2) - G''(0)$ and $G''(3) - G''(0)$ respectively. A much more plausible interpretation of these observations is that the lines are really lines of a resonance fluorescence series. The wave-number of the exciting line is 17014·8 cm.$^{-1}$ There is only one[11] strong absorption band in this region, 13,2 of B − X, with head at 17033·7 cm.$^{-1}$ The 'Raman spectrum' may then be interpreted as the series dropping from $v' = 13$ to $v'' = 2$, 3, 4 and 5. The anti-Stokes lines are presumed not to have been observed on account of re-absorption. The numerical evidence in support of this interpretation is as follows:-

Observed shift	Calculated Raman shift		Calculated resonance shift	
316·8 cm.$^{-1}$	$G''(1)-G''(0)$	321·5	$G''(3)-G''(2)$	316·9
631·3	$G''(2)-G''(0)$	640·7	$G''(4)-G''(3)$	631·5
944·5	$G''(3)-G''(0)$	957·6	$G''(5)-G''(4)$	943·8

The calculated values are with $G'' = 323{\cdot}81\,(v'' + \tfrac{1}{2}) - 1{\cdot}15\,(v'' + \tfrac{1}{2})^2$.

Features other than bands of the B − X system of bromine appear in emission in certain sources. As well as the visible continuum already mentioned,[28,29] there readily appear ultra-violet continua. A continuum at 2900 A. is excited by the action of active nitrogen on bromine vapour[38] and continua with long wave-length limits at 3700 and 2950 A. are observed[39] when bromine is excited in the Tesla discharge. The 2900 A. continuum has also been observed in the electrodeless discharge,[40] in the spectrum of methyl bromide − oxygen flames,[27] and in absorption[35] (see page 780).

The longer wave-length ultra-violet continuum, $\lambda \geqslant 3400$ A., has been observed in flames.[41] Earlier observations of these continua are summarized and discussed by Finkelnburg.[42,43] The spectrum of the electrodeless discharge has recently been examined in detail by Venkateswarlu.[44] He has found that the continua in the region 2000 to 4400 A. show vibrational structure, and interprets them as arising from transitions from stable upper states to repulsive lower states arising from $^2P_{3/2} + {}^2P_{3/2}$, $^2P_{3/2} + {}^2P_{1/2}$ and $^2P_{1/2} + {}^2P_{1/2}$ atom pairs. The transitions have been discussed[45] in the light of Mulliken's predictions.[47] The stronger maxima lie at 2480, 2625, 2755, 2900, 3337 and 3550 A. The constants for the upper states are as follows:-

State	T_0	ω
F ($\Pi_{2,1}$)	66600	480 cm.$^{-1}$
E ($^1\Pi_g$)	61400	220
D ($^2\Pi_{1g}$)	55535	330
C ($^3\Sigma_u^+$)	47000	−

Further experimental information about these states is desirable.

Two transitions, apparently unrelated to any state so far discussed, have been observed in emission from a discharge-tube.[46] They consist of two systems of red-degraded bands in the region 5100 to 6600 A. Rather doubtful vibrational analyses lead to the following expressions for the band-heads:-

$$\text{I}\quad \nu = 17325{\cdot}8 + 191{\cdot}45\,u' - 1{\cdot}05\,u'^2 - 360{\cdot}6_5\,u'' + 0{\cdot}65\,u''^2$$
$$\text{II}\quad \nu = 16105{\cdot}0 + 152{\cdot}4\,u' - 0{\cdot}40\,u'^2 - 361{\cdot}7_0\,u'' + 1{\cdot}62\,u''^2,$$
$$\text{where } u = v + \tfrac{1}{2}.$$

Mulliken[47] has suggested that the emitter of these bands may be the molecule-ion, Br_2^+.

The quantitative aspects of the absorption continua of bromine (see Table IV) raise a number of interesting problems which have been much investigated.[1,48-50] A detailed investigation[51] of the extinction coefficients in the Q,N continuum from 3275 to 5720 A. at temperatures between 20 and 632°C. shows that the continuum can be resolved into two overlapping continua, *A* and *B*. The theoretical treatment of Mulliken[21] leads to the alternative interpretations:-

	I Upper state			II Upper state
Continuum *B*:	$\begin{cases} ^3\Pi_1 \\ ^3\Pi_{0+} \end{cases}$	or	*B*:	$^3\Pi_1$
A:	$^1\Pi_u$		*A*:	$\begin{cases} ^3\Pi_{0+} \\ ^1\Pi \end{cases}$

In (I) the transition to $^3\Pi_1$ is very weak compared with the other two, and in (II) the transitions to $^3\Pi_1$ and $^3\Pi_{0+}$ should be of about equal intensity, and each about two-fifths as strong as the transition to $^1\Pi$. The problem of choosing the correct interpretation has been attacked by deriving the course of the upper state potential curves in the repulsive regions,[52] making use of the experimental information about the variation of extinction coefficient with frequency and of the data for the ground state, and fitting the repulsive curve to the extrapolated potential curve[53] for the state $^3\Pi_{0+u}$. This procedure demands an accurate potential function for $^3\Pi_{0+u}$ and Rees[54] has given analytical expressions equivalent to the Rydberg-Klein construction (see [34]). The potential energy curve for the $^3\Pi_{0+}$ state is found to extrapolate smoothly to the curve deduced from the continuum *B*, and it thus appears that interpretation (I) is correct.[22] The $^1\Pi_u$ state correlates with ground-state atoms, $^2P_{3/2} + {}^2P_{3/2}$, and it may be responsible for the perturbations observed in $v' = 3,4$ of $^3\Pi_{0+}$.

The effect of temperature on the distribution of intensity in the *A* and *B* continua is quite simply, and successfully, represented by expressions developed by Sulzer and Wieland.[55]

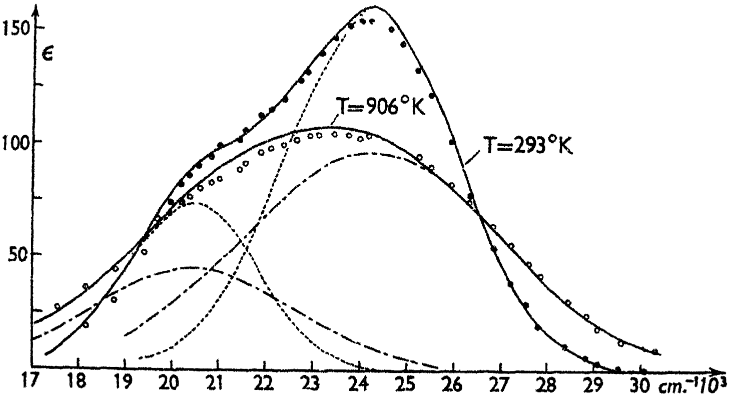

Fig. 2. ABSORPTION CURVE FOR Br_2

- - - - - - - - - -	Calculated values for $T = 293$°K.
-·-·-·-·-·-·-·-·-	Calculated values for $T = 900$°K.
————————	Graph of calculated total absorption.
•••••••••••••••••• oooooooooooooooooo	Points as determined by Acton *et al.*[51] at $\begin{cases} 293°K. \\ 906°K. \end{cases}$

At shorter wave-lengths, bromine vapour becomes more transparent, and there is a minimum at about 3000 A., with $\epsilon \sim 0{\cdot}2$. Thereafter the extinction coefficient rises again,[20] to a weak maximum at about 2250 A., with $\epsilon_{\max} \sim 3{\cdot}5$.

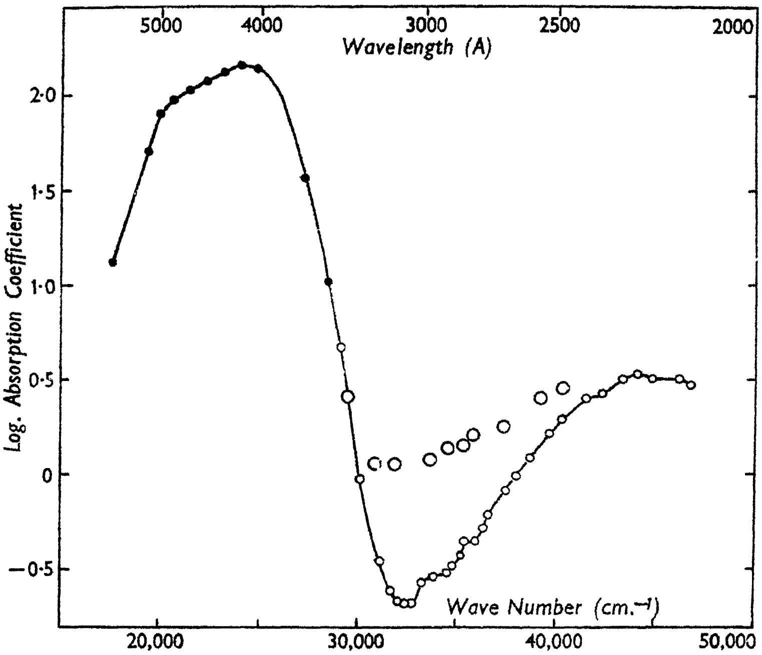

Fig. 3. LOG ϵ FOR BROMINE PLOTTED AGAINST WAVE NUMBER IN THE VISIBLE AND ULTRA-VIOLET

Cordes and Sponer[18] have observed continuous absorption in the Schumann region. On theoretical grounds, there is expected[19] to be a strong transition, V, $^1\Sigma_u^+ \leftarrow$ N, $^1\Sigma_g^+$, with $\nu_{\max} \sim 64000$ cm.$^{-1}$

The visible absorption spectrum of bromine vapour has also been studied from other points of view. The absorption in the region of the line Hg 5461 A. has been studied interferometrically:[56] this is of interest in connexion with the fluorescence excited by that line (see above). The absorption in the region 5770 to 5790 A. has been examined[57] at different pressures and temperatures; anomalous dispersion in this region has also been studied.[69] The effect of foreign gas on extinction coefficients in the *A*, *B* and *C* continua has been investigated.[58] Intensities in the *A* and *B* continua are increased moderately: in increasing order of effect are N_2, O_2, He, HBr, CO_2, HCl, Ne. There is no appreciable displacement of the maximum. The *C* continuum is however very sensitive to the presence of foreign gases, and its intensity may be increased very greatly.

A number of investigators,[48,59-64,70] have attempted to measure extinction coefficients in the region of banded absorption at $\lambda > 5100$ A., with discordant results (for a full bibliography, see Kortüm and Müller[64,65]). These variations are attributed to changes in the line-breadths with pressure.[66] The apparent extinction coefficients which have most often been measured relate to groups of rotational lines whose profiles change with changing pressure.[67] From the variation of apparent extinction coefficient with pressure, it is possible to calculate a value for the optical collision diameter: Kortüm and Luck[66] obtain 7·66 A., about 1·3 times the kinetic theory collision diameter. The effect of foreign gas is to increase, in the banded region, the value of the apparent extinction coefficient: this has been attributed[60,68] to a collision-induced predissociation, and to an increase of the transition probability,[65] but it now appears that this too may largely be attributed to normal line-broadening effects.[65]

The absorption spectrum of liquid bromine has been studied:[71,72] the shape[73] of the absorption curve in the region of the *A*,*B* continua is much the same in the liquid as it is in the gas, but ϵ_{max} for the liquid is here about twice that for the gas. However, the ultra-violet absorption of the liquid (continuum *C*) is vastly more intense in the liquid: it was followed to 45000 cm.$^{-1}$ where $\epsilon \sim 10^3$.

The absorption spectrum of bromine crystals has been examined:[74] it was found that at 20°K. there are three absorption bands at 5000 to 4700, 4300 to 4100 and 3700 to 3600 A., of which the middle band is the most intense. At liquid nitrogen temperatures, there appeared only one band at 4300 to 3600 A., with continuous absorption below 3240 A.

The absorption of light by bromine adsorbed on calcium fluoride has been studied.[75] The spectrum is shifted to shorter wave-lengths as compared with that in the gas, and there appear two maxima, at 2670 and 2520 A. (see also reference [76]).

The absorption spectra of solutions containing bromine have attracted attention.[77-83] A summary of the results is given in Table V. With inert solvents, the shape of the *A*,*B* continua is little changed in solution from its shape in the gas, although the value of ϵ_{max} is always larger in solution - in the case of carbon disulphide, about three times as large. In water and alcohol there is a pronounced shift to shorter wave-lengths. The ultra-violet continua are always much stronger in solution than in the gas (as with liquid bromine, see above) and in the aromatic solvents the continua are very strong indeed. Interpretations of these facts have been put forward on the following lines:-

TABLE V. - THE ABSORPTION SPECTRA OF BROMINE SOLUTIONS

Solvent	*A*,*B* continua		Ultra-violet continua		Reference
	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}	
(Gas)	4150	155	2250	3·5	(see Table IV)
Carbon tetrachloride	4170	208			78
	4170	242			80
	4170	205	<2780	>68	81
Chloroform	4130	212			80
	4100	205	<3000	>200	81
Carbon disulphide	4195	441			80
*cyclo*Hexane	4200	210	<2860	>460	81
Acetic acid	4070	220			80
Ethyl alcohol	3710	235			80
Water	3980	226			80
	3930	164	<2780	>105	81
Benzene	4140	334			80
	4150	310	2930	6800	81,84
Chlorobenzene	4100	265	2960	<6800	81,85
Toluene	4150	360	2975	>6800	81,85

(i) the effect of the cage of solvent molecules.[82,83,86,87]
(ii) the effect of electrostatic polarization.[84,88]
(iii) the formation of complexes, Ar,Br_2, between bromine and aromatic molecules.[85]

The displacement of the A,B continua in associated solvents is discussed in terms of the cage effect. Work must be done to increase the internal surface area of the cage around the solute molecules to accommodate the molecule of radius r_e''. If the solvent is regarded as forming a semi-rigid cage of radius h, then the potential barrier may be written as:-

$$W''(r) = 4\pi\gamma\,(r^2 - h^2)$$

where γ is the surface free energy per unit area. The potential energy of the dissolved molecule is then:-

$$U_s''(r) = U_g''(r) + W''(r)$$

where $U_g''(r)$ is the potential energy function for the gaseous molecule. For bromine in water, Rees[87] obtained $(r_e'')_s = 2{\cdot}255$ A., *i.e.* 0·03 A. less than in the gas. The minimum lies 990 cm.$^{-1}$ higher than in the gas. The shift in the value of ν_{max} for the A continuum is calculated to be 1400 cm.$^{-1}$ as compared with 1750 cm.$^{-1}$ observed. The effects of temperature have also been treated according to this model.[82,83]

Bayliss[88] has discussed the shifts to longer wave-lengths occurring on solution which arise from the electrostatic polarization of the solvent. He suggests that the intense band at 2900 A. which appears when bromine is dissolved in benzene is to be ascribed to the V-N transition expected in the gas at about 64000 cm.$^{-1}$ (see Table IV): the shift would thus amount to about 30000 cm.$^{-1}$ if this view is correct.

Mulliken[85] prefers to regard the 2900 band found in the aromatic solutions as the charge-transfer spectrum of a 1:1 complex, Ar,Br_2, analogous to the iodine complexes (see page 79) whose existence seems now to be established beyond doubt.

The electron configurations in the ground and excited states of the bromine molecule have been treated in detail.[47,89] The predicted value[47] for the lowest ionization potential (without change of internuclear distance) is 12·27 eV. The absolute intensities in the O,N transitions have been considered.[19,21] The possibility of an electron affinity spectrum has been discussed.[90] An improved potential energy function for the ground state of the bromine molecule has been derived,[91] using the experimental values of the energy of dissociation, r_e'', ω_e'', $x_e''\omega_e''$ and α_e'': it lies somewhat above the Morse potential curve. A potential function $V = (a/r^m) - be^{-nr}$ has been examined.[92] Interrelations between the force constant, internuclear distance and energy of dissociation have been discussed.[93] Thermodynamic functions for gaseous bromine in the range 200 to 1600°K., and equilibrium constants for the dissociation $Br_{2g} \rightarrow 2Br_g$ between 298 and 1600°K. have been evaluated.[94]

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IODINE MONOBROMIDE, IBr

Only the electronic spectrum of iodine monobromide has so far been studied. The first information about this spectrum came from the work of Badger and Yost,[1] who observed a system in absorption lying in the infra-red region between 6850 and 8060 A. Cordes[2] found a number of absorption bands between 5500 and 6350 A., and two regions of continuous absorption with λ_{max} equal to 4050 and 4950 A. Both sets of bands were subsequently studied by Brown[3] with high resolving power: he was able to separate isotopic heads of $I^{79}Br$ and $I^{81}Br$. There are three absorption band-systems in the region 5450 to 8100 A. which arise from transitions from the ground-state, X $^1\Sigma^+$, to A $^3\Pi_1$, B $^3\Pi_{0+}$ and B′ 0^+. The state B′ 0^+ results from the interaction between B $^3\Pi_{0+}$ (from I $^2P_{3/2}$ + Br $^2P_{1/2}$) and a repulsive state 0^+ (from the ground-state atoms, I $^2P_{3/2}$ + Br $^2P_{3/2}$). A similar situation occurs in iodine monochloride (see page 635). The continua at 4950, 4050 A. are then ascribed to transitions from the ground state, X $^1\Sigma^+$, to repulsive portions of the potential-energy curves for B $^3\Pi_{0+}$ and B′ 0^+ respectively. Predissociation is observed in B $^3\Pi_{0+}$ at $v' = 6$, and there are a number of intensity anomalies arising from the B − B′ interaction.

The absorption spectrum of iodine monobromide has also been studied in the Schumann region,[4,5] two band-systems, C,D ← X, have been found. Light from the aluminium spark excites a fluorescence spectrum[6] in the vapour of iodine monobromide consisting of bands in the region 2890 to 4850 A.: the addition of nitrogen causes a colour change from violet to blue. Loomis and Allen,[7] who examined the fluorescence excited by Hg 1849 A., found that the strongest lines could be represented by $\nu = 58048 - 276{\cdot}2\,p + 1{\cdot}28\,p^2$, with p integral. The odd terms could be followed as far as $p = 43$. The line structure ceases at about 2500 A., but diffuse headless bands are observed as far as 3700 A. A detailed interpretation of these results is lacking, but it is clear that the C − X transition may be excited in fluorescence. Some of the longer-wave-length fluorescence bands may correspond to the bands observed in emission in a discharge tube.[8] Continua are also observed in this source with λ_{max} at 5059 and 5153 A., and a number of diffuse bands between 2300 and 4800 A. This emission spectrum is thought to arise from transitions from stable upper electronic states to sets of repulsive states, as in the case of iodine monochloride (see page 635). Constants[3,5,9] for the electronic states of iodine monobromide are given in Table VI.

The state A $^3\Pi_1$ dissociates to give unexcited atoms, I ($^2P_{3/2}$) + Br ($^2P_{3/2}$): the convergence limit has been determined very precisely[3] as 14660 ± 5 $cm.^{-1}$, corresponding to an energy of dissociation, D_0 (IBr) equal to $41{\cdot}90_5 \pm 0{\cdot}01_5$ kg.-cal. The results of thermochemical studies are in good agreement with this value.[11] For example, McMorris and Yost[12] found, from equilibrium measurements, Q_f (IBr_g) = 9·96 kg.-cal.: with Q_f (I_g) = 25·48; Q_f (Br_g) =

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TABLE VI. - CONSTANTS FOR IODINE MONOBROMIDE ($I^{79}Br$), CM.$^{-1}$

State	T_0	ω_e	$x_e\omega_e$
D (II)	56370	$\Delta G_{1/2} = 310$	
C (II)	51700	$\Delta G_{1/2} = 314$	
$B'\ 0^+$	16776	60	–
$B\ ^3\Pi_{0+}$	16095	150	4·3
$A\ ^3\Pi_1$	12166	140	1·9
$X\ ^1\Sigma^+$	0	268·4	0·78

Notes:-

(1) There is a little uncertainty about some of these figures.[9]

(2) The internuclear distance in IBr has not been determined: an estimate is[10] $r_e'' = 2{\cdot}43$ A.

26·71 kg.-cal.,[13] D (IBr) = 42·2$_3$ kg.-cal. at 25°C.; this is equivalent to D_0 (IBr) = 41·5$_8$ kg.-cal. at 0°K.

Thermodynamic properties of gaseous iodine monobromide, and equilibrium constants for the dissociation into molecular and atomic iodine and bromine have been calculated[10] over the range 298·16° to 2000°K. The electronic states of iodine monobromide, like those of the other halogen molecules, have formed the subject of detailed theoretical work by Mulliken. He has predicted the existence of a number of low-lying electronic states,[14,15] has estimated ionization potentials,[14] and has made calculations of the absolute intensities of the visible absorption systems.[16,17] The present experimental information about the spectrum of iodine monobromide is as yet inadequate in many respects for detailed comparison with the theoretical conclusions. The states C,D (called by Mulliken B,C) are considered to arise from the configurations $[I^+Br,\ ^2\Pi_{3/2}]\sigma^X$ and $[I^+Br,\ ^2\Pi_{1/2}]\sigma^X$ with JJ-like coupling between the I^+Br core and the σ^X excited electron.

The absorption spectrum of iodine monobromide dissolved in carbon tetrachloride has been examined,[18] and more detailed studies in a number of different solvents were later carried out.[19] Solutions in inert solvents such as carbon tetrachloride, trichloroethylene, hexane, *cyclo*hexane, benzene and toluene, are red. In carbon tetrachloride, the main absorption band has $\lambda_{max} = 4900$ A., $\epsilon_{max} = 390$: there is a second band with $\lambda_{max} = 2660$, $\epsilon_{max} = 200$. The figures for other inert solvents are similar. In the case of oxygenated solvents such as alcohols, acids, esters, ethers and ketones, the main absorption band is shifted to shorter wave-lengths[20] and the solutions are yellow or orange, thus:-

Solvent	λ_{max}, A.	ϵ_{max}
Ethyl alcohol	3900	390
Ethyl acetate	3950	390
Acetic acid	4190	350

It seems that in these solutions rather stable complexes are formed in which the structure differs little from that of a normal valence compound of oxonium type.[21]

Solutions of iodine monobromide in aqueous hydrogen bromide and hydrogen chloride show quite new absorption bands: for example:-

	λ_{max}, A.	ϵ_{max}
IBr in HBr	3750	590
	2535	50400
IBr in HCl	3610	320

These bands are attributed to ions IBr_2^- and $IClBr^-$ respectively.[19]

The relation between force constant and ionic polarizability has been considered.[22] Calculations have been made[22] of the bond-moment in iodine monobromide, using an ionic-covalent resonance treatment.

The absorption of *X*-rays by gaseous iodine monobromide in the region of the *K*-edge for bromine has been studied.[24] There is a pronounced structure near the short-wave-length side similar to that observed in the case of gaseous bromine (see page 774).

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HYDROGEN BROMIDE

The pure rotation spectrum of hydrogen bromide was first observed in the notable series of experiments carried out by Czerny,[1] who measured the lines with $J'' = 4$ to 13 lying between 83 and 230 cm^{-1}.[1] This spectrum has recently been studied again,[2] with results in good agreement with the earlier measurements.

The transition $J = 1 \leftarrow 0$ has now been observed for DBr under high resolution[3] in the micro-wave region. Isotope and nuclear quadrupole effects combine to split the transition into six lines. In the present case, the separations of the observed levels, perturbed by nuclear quadrupole effects, from the unperturbed level for a given isotopic molecule are given by:-[52]

$$E_q = -\,eOq\,Y(F),$$

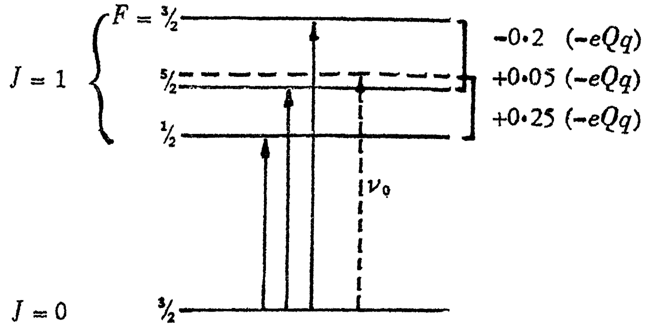
$$\text{with}\quad Y(F) = \frac{\tfrac{3}{4}C(C+1) - I(I+1)J(J+1)}{2J(2J-1)2I(2I-1)}$$

$$\text{where}\quad C = F(F+1) - I(I+1) - J(J+1),$$

$$\text{and}\quad F = J+I,\ J+I-1,\ \cdots,\ J-I.$$

In the present case, we have $I = 3/2$ for both ^{79}Br and ^{81}Br. Thus the transition may be represented as in the diagram at the head of the next page.

The results for $D^{79}Br$ (frequencies in Mc./sec.) are given below the diagram.



J	F	$Y(F)$	ν_{observed}	$532{\cdot}9\ Y(F)$	ν_0
$1\leftarrow 0$	$3/2\leftarrow 3/2$	$-0{\cdot}2$	254 811·8	$-106{\cdot}6$	254 705·2
$1\leftarrow 0$	$5/2\leftarrow 3/2$	$+0{\cdot}05$	254 678·5	$+\ 26{\cdot}6$	254 705·1
$1\leftarrow 0$	$1/2\leftarrow 3/2$	$+0{\cdot}25$	254 572·0	$+133{\cdot}2$	254 705·2

It will be seen that constant values of ν_0 are obtained with $eQq = +532{\cdot}_9$ Mc./sec. For $D^{81}Br$, the corresponding values are $\nu_0 = 254\ 548{\cdot}_9$ and $eQq = +444{\cdot}_9$ Mc./sec. ν_0 is equal to $(2B-4D)$, where B is the rotational constant dependent on the reciprocal of the moment of inertia of the molecule, and D is the centrifugal stretching constant (see page 230). Values of D have been found[4] from observations on the vibration-rotation bands of DBr. For both molecules, $4D = 11{\cdot}4$ Mc./sec., so that:-

$$B_0\,(D^{79}Br) = 127\ 358{\cdot}3 \text{ Mc./sec.};\quad B_0\,(D^{81}Br) = 127\ 280{\cdot}_2 \text{ Mc./sec.}$$

B_e is given by $B_e = B_0 + \alpha/2$. Again, values of α may be taken from the results of the infra-red work; in this case, however, α is not known sufficiently well for the full accuracy of the micro-wave results to be exploited. For $D^{79}Br$, $\alpha = 2515{\cdot}_2$, and for $D^{81}Br$, $\alpha = 2512{\cdot}_2$ Mc./sec., and B_e $(D^{79}Br) = 128\ 616$, B_e $(D^{81}Br) = 128\ 536$ Mc./sec. Finally, r_e is given by:-

$$r_e = (5{\cdot}05480 \times 10^5/B_e\,\mu)^{1/2},$$

where B_e is in Mc./sec., and μ, the reduced mass, is in atomic mass units. With $\mu\,(D^{79}Br) = 1{\cdot}964\ 571$, $\mu\,(D^{81}Br) = 1{\cdot}965\ 778$:-

$$r_e\,(D^{79}Br) = 1{\cdot}414\ 4_0,\ r_e\,(D^{81}Br) = 1{\cdot}414\ 4_0 \text{ A.}$$

The number of unbalanced p electrons of bromine in deuterium bromide, U_p, may be estimated as $U_p = (eQq)_{\text{molecular}}/2(eQq)_{\text{atomic}}$. The value of $(eQq)_{\text{atomic}}$ has been determined from atomic beam experiments.[5] Hence $U_p = 0{\cdot}69$, which may be interpreted as indicating that the bond in gaseous deuterium bromide has about 31% ionic character.

The fundamental vibration-rotation band of hydrogen bromide lies at about 3·91 μ. The observation of this band, and of the analogous bands of the other hydrogen halides,[6] aroused much theoretical comment:[7-12] however the correct interpretation of these spectra could not be given until wave-mechanical theory was established.[13] In later work, attention has been directed both to the study of overtone bands and to the use of higher resolving power. Plyler and Barker[14] measured lines of the $1-0$ and $2-0$ bands, and were able just to detect the isotope effect between $H^{79}Br$ and $H^{81}Br$. Naudé and Verleger[15] measured seven lines of the $4-0$ band for each isotopic species. The isotope effect in the $1-0$ band of HBr was clearly resolved by Thompson, Williams and Callomon,[16] and in the $1-0$, $2-0$ and $3-0$ bands of DBr by Keller and Nielsen.[4] Rotational and vibrational constants for the ground state of the hydrogen bromide molecule are collected together in Table VII. Although the main constants are now known quite well, uncertainties in the values of $y_e\omega_e$, α_e, D_e and β may be considerable.

TABLE VII. - SPECTROSCOPIC CONSTANTS FOR HYDROGEN BROMIDE

Species:	$H^{79}Br$	$H^{81}Br$	$D^{79}Br$	$D^{81}Br$	Dependence on ρ
ω_e	2648·619	2648·204	1885·327	1884·748	ρ^1
$x_e\omega_e$	44·865	44·850	22·732	22·718	ρ^2
$y_e\omega_e$	−0·0294	−0·0294	−0·0106	−0·0106	ρ^3
B_e	$8{\cdot}469_0$	$8{\cdot}466_5$	$4{\cdot}290_8$	$4{\cdot}287_6$	ρ^2
α_e	$0{\cdot}231_3$	$0{\cdot}231_3$	$0{\cdot}083_9$	$0{\cdot}083_8$	ρ^3
D_e	$3{\cdot}90_5 \times 10^{-4}$	$3{\cdot}90_7 \times 10^{-4}$	$9{\cdot}6_4 \times 10^{-5}$	$9{\cdot}5_9 \times 10^{-5}$	ρ^4
β_e	-8×10^{-6}	-8×10^{-6}	$-2{\cdot}_2 \times 10^{-6}$	$-2{\cdot}_2 \times 10^{-6}$	ρ^5
r_e, A.	$1{\cdot}414\ 4_0$				
μ,a.m.u.	$0{\cdot}995\ 411_5$	$0{\cdot}995\ 721_5$	$1{\cdot}964\ 57_1$	$1{\cdot}965\ 77_8$	

Notes:-

(1) The meaning of these quantities may be illustrated by the following relations for $H^{79}Br$:-

$$G_v = 2648{\cdot}61_9\,(v+\tfrac{1}{2}) - 44{\cdot}86_5\,(v+\tfrac{1}{2})^2 - 0{\cdot}029_4\,(v+\tfrac{1}{2})^3.$$

$$B_v = 8{\cdot}469_0 - 0{\cdot}231_3\,(v+\tfrac{1}{2}).$$

$$D_v = [3{\cdot}90_5 - 0{\cdot}0_8\,(v+\tfrac{1}{2})] \times 10^{-4}.$$

(2) $\rho = (\mu/\mu_i)$, with μ the reduced mass.

(3) The vibrational constants are from Keller and Nielsen.[4] The rotational constants for HBr are from Thompson, Williams and Callomon,[16] those for DBr from Keller and Nielsen.[4] These two sets of constants are however not quite compatible.

(4) The value of r_e has been calculated from the data on the microwave spectrum of DBr (see page 790).

The Raman effect in gaseous hydrogen bromide was observed:[17] shifts were found at 2556 cm.$^{-1}$ from Hg 4047 and 4358 A. The Raman 'line' really consists of a more or less broad Q branch, with a maximum at 2550 cm.$^{-1}$, and a long-wave-length edge[18] (near to $Q = 0$) at 2558 cm.$^{-1}$ This is in excellent agreement with the value $2558{\cdot}5_8$ cm.$^{-1}$ expected from infra-red measurements.[16]

In liquid hydrogen bromide,[18] the Raman frequency is smaller: the long-wave-length edge drops to about 2487, and the maximum to 2466 cm.$^{-1}$ The Raman spectrum of the crystal at 155°K. is similar.[19] This displacement of the frequency in the crystal to values lower than for the free gas has also been studied in the infra-red region:[20] in the low-temperature phase, two peaks are observed[67] (see page 643). The displacement decreases as the temperature is increased.

Similar displacements are observed in the Raman spectra of hydrogen bromide dissolved in various solvents.[21,22] Representative values are as follows:-

Solvent	Frequency, cm.$^{-1}$
(Gas)	2558
Carbon tetrachloride	2519
Chloroform	2500
(Liquid)	2466
Chlorobenzene	2483
Ethyl bromide	2471
Benzene	2453

Although these effects are probably more complex than will admit of any simple interpretation, some correlation with the low frequency dielectric constant of the solvent is suggested.

Refs. p. 795

Concentrated solutions of hydrogen bromide in ionizing solvents such as ethyl alcohol, diethyl ether and acetic acid have no features which can be interpreted as arising from a vibration H–Br in an independent diatomic molecule.[21] The Raman spectrum of hydrogen bromide in diethyl ether at –40°C. has been discussed in terms of the formation of a molecular compound.[23] Concentrated aqueous solutions of hydrogen bromide show, as do those of other acids, infra-red absorption bands at 2·3, 2·55 and 5·5μ not given by water alone.[24,28] In crystalline HBr,H_2O the only spectrum observed[68] is that of the oxonium ion, H_3O^+.

The determination of the intensities of infra-red transitions is of great interest because of the information they may give about the polar properties of the absorbing molecule. Rosenthal[26] calculated the *relative* intensities of the second, third and fourth overtone bands of hydrogen bromide with respect to the fundamental, assuming a Morse potential function: as in the case of hydrogen chloride, her estimates are too high. Bartholomé[27] attempted to measure the *absolute* intensity of the fundamental band: however, his result is very low, probably because he used inadequate spectral resolving power.[28] The absolute intensities of the fundamental and first overtone bands have recently been measured very carefully by Penner and Weber.[29] They obtain:-

$$\alpha_F \ (1-0 \text{ band}) = 55 \pm 15 \text{ cm.}^{-2} \text{ atm.}^{-1}$$
$$\alpha_0 \ (2-0 \text{ band}) = 0{\cdot}70 \pm 0{\cdot}30$$

at 297 ± 2°K. From these values, the variation of electric moment, $p(\xi)$, with displacement, $\xi = (r - r_e)/r_e$, where r is the internuclear distance, was found to be:-

$$p(\xi) = p_e^0 \pm [0{\cdot}820 \times 10^{-18}\xi + (1{\cdot}83 \times 10^{-18}\xi^2 \text{ or } -0{\cdot}169 \times 10^{-18}\xi^2)].$$

(For the relation between $p(\xi)$ and α, see Crawford and Dinsmore,[30,31] also page 641). The refractive index of hydrogen bromide and of deuterium bromide has been measured in the visible and ultra-violet regions,[32] but observations in the infra-red, which could be used to check the absolute intensities of the absorption bands, do not appear yet to have been made.

Transmission measurements in the region of the fundamental band of hydrogen bromide have been made:[33] however, as in the case of hydrogen chloride (see page 643), the transmission proves to be a non-linear function of the total pressure, so that the simple theories of collision broadening are inapplicable. The factors governing the emissivity of gaseous hydrogen bromide in the infra-red region have been discussed.[34]

The emission spectrum of hydrogen bromide in the region of the fundamental band has been studied.[35] The source was a hydrogen-bromine flame. In addition to lines of the 1 – 0 band, a number of lines of the 2 – 1 band were observed. Rotational temperatures of 1400 ± 70°K. were found for both bands: the vibrational temperature was estimated to be 1400 ± 125°K. Thus in the region of the flame examined, there appears to be equilibrium between the rotational and vibrational modes of excitation.

The spectrum of a discharge in gaseous hydrogen bromide[36-40] contains no discrete electronic bands attributable to this molecule in the region above 2000 A., but, according to the conditions, various continua or the $^2\Sigma - {}^2\Pi_i$ system of the molecule-ion HBr^+ (*q.v.*), may be excited. Although the continua, of which the most characteristic have λ_{max} = 3480 and 2870 A., have been interpreted as arising from transitions from repulsive upper states to the ground state either of the molecule-ion[36] or of the molecule,[36,38,39] it is in fact by no means certain that either species is responsible for the emission.[40]

The ultra-violet absorption spectrum of gaseous hydrogen bromide is continuous at wave-lengths down to about 1500 A. Early investigations[36,41-3,45] were confined to wave-lengths above 2000 A., and several attempts were made to establish a correlation between the long-wave-length limit of the absorption continuum and the dissociation energy. However, this limit is not sharp, and it is not surprising that it is given variously as 2640,[36] 3260,[41] 3090[42] and 2700 A.[45] Information about the dissociation energy may properly be obtained from such measurements only by computing the course of the potential energy curve for the upper repulsive state.[44,46,49] The most careful and extensive sets of measurements of the extinction coefficient are those of Goodeve and Taylor[46] and of Romand.[47-9] The former cover the range 1800 to 2850 A., the latter 1400 to 2300 A. The agreement between the two is good except that the extinction coefficients of Goodeve and Taylor at the low wave-length end of their range are somewhat higher than those of Romand (see Fig. 4).

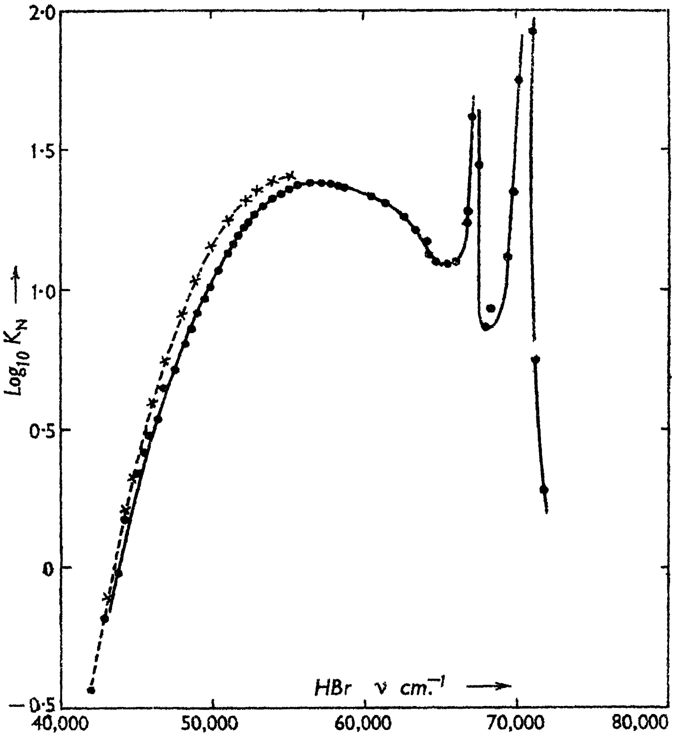


Fig. 4. ABSORPTION SPECTRUM OF HBr IN THE ULTRA-VIOLET

Both Goodeve and Taylor,[46] and Romand,[49] have made approximate calculations of the shape of the potential curve for the repulsive upper state. Since the dissociation energy of the ground state of hydrogen bromide is known (see page 795), it is possible to identify the states of the atoms to be correlated with the upper molecular state: they prove to be ground states, H($^2S_{1/2}$) + Br($^2P_{3/2}$). It may be, however, that more than one upper molecular state is responsible for the absorption in this region (see page 794): the present experimental data do not suffice to resolve this question.[49]

The discrete absorption bands (Fig. 4) were measured earlier by Price.[50] They arise by transitions to two states B and C separated by an interval related to the interval $^2\Pi_{1/2}$ - $^2\Pi_{3/2}$ in the ground state of the ion HBr$^+$. Similar bands are observed in the methyl halides which lead on to Rydberg series. By a comparison of the positions of the states B and C in hydrogen bromide with the term-values of the analogous states in methyl bromide, Price was able to derive a value for the ionization potential of hydrogen bromide, later corrected[51] to $12{\cdot}1_0$ eV., or $279{\cdot}_0$ kg.-cal./mole. The constants for the states B and C are as follows.-

	T_0	ω_e	$x_e\omega_e$
C ($^1\Pi$)	70542	2506	58 cm.$^{-1}$
B ($^1\Pi$)	67084	-	-

Mulliken[53,54] has considered the electronic states of hydrogen bromide in some detail. The ultra-violet absorption continuum[55] arises from a valence-shell transition involving the transfer of an electron from a nearly non-bonding π orbital to an anti-bonding σ orbital, thus:-

$$\text{Q: } \sigma^2.\pi^3_{\text{Br}}\sigma^*,\ {}^3\Pi, {}^1\Pi \leftarrow \text{N: } \sigma^2\pi^4_{\text{Br}},\ {}^1\Sigma^+.$$

The allowed transitions from N $^1\Sigma^+$ are to Q $^3\Pi_1$, $^3\Pi_{0+}$, $^1\Pi$, but it is probable that in hydrogen bromide most of the intensity is in the transitions Q $^3\Pi$, $^1\Pi \leftarrow$ N. Both $^1\Pi$ and $^3\Pi_1$ arise from ground-state atoms H($^2S_{1/2}$) + Br($^2P_{3/2}$), but $^3\Pi_{0+}$ correlates with H($^2S_{1/2}$) + Br($^2P_{1/2}$).

The absolute intensity of the Q$\leftarrow$N transition may be determined, both theoretically and experimentally.[55,56] If K_ν is the absorption coefficient defined by $I_\nu = I^0_\nu.e^{-K_\nu l}$, with l the length of absorption path in cm. (K_ν is, for a gas at 0°C. and 1 atm. pressure, related to the molar decadic extinction coeffieient, ϵ_ν, defined by $I_\nu = I^0_\nu.10^{-\epsilon_\nu cl}$, with c in moles/litre, by $K_\nu = 0{\cdot}1028\ \epsilon_\nu$), then the dipole strength, D, for the transition is given by:-

$$\begin{aligned} D &= (3hc/8\pi^3Ne^2)\int\gamma.K_\nu.d\nu/\nu \\ &= 3{\cdot}88 \times 10^{-19} \int\gamma.K_\nu d\nu/\nu \end{aligned}$$

For a gas, $\gamma = n$ (refractive index) $\simeq 1$.

In the case of hydrogen bromide, Mulliken finds, from the data of Goodeve and Taylor,[46] $D(\text{N,Q}) = 0{\cdot}058$ A^2. Values interpolated between the results calculated for the corresponding transitions in hydrogen chloride and hydrogen iodide are 0·19 according to an atomic orbital approximation, and 0·098 according to a linear combination of atomic orbitals (molecular orbital) approximation.

The states B and C found by Price at shorter wave-lengths are represented[54] as follows:-

$$\begin{aligned} &\text{C: } (\sigma^2\pi^3,\ {}^2\Pi_{1/2})b\sigma \\ &\text{B: } (\sigma^2\pi^3,\ {}^2\Pi_{3/2})b\sigma \end{aligned}$$

with JJ-like coupling between the σ electron and the HBr$^+$ ion core.

The ionization potential for the process:-

$$\sigma^2\pi^4 \rightarrow \sigma^2\pi^3,\ {}^2\Pi$$

was predicted[57] to be 12·43 eV. (for the mean of the $^2\Pi_{3/2}$, $^2\Pi_{1/2}$ states of the ion). Correcting this to give the ionization potential to $^2\Pi_{1/2}$ of HBr$^+$, there is obtained 12·27 eV., in good agreement with the experimental value, $12{\cdot}1_0$ eV.

The bond moment in hydrogen bromide has been calculated by an ionic-covalent resonance treatment.[58] What seems to be a rather naive attempt has been made to correlate the position of the ultra-violet absorption bands with the ionic character in the hydrogen halides.[59] Potential energy functions for the ground-state of hydrogen bromide have been examined.[60,61] Relations between force-constant and internuclear distance have been considered.[62,63] Fajans[64] has discussed the electron affinity of hydrogen bromide.

The dissociation energy of hydrogen bromide cannot be obtained directly from present spectral information.[65] It may be derived from the heat of formation[66] thus:-

$$\begin{aligned} \tfrac{1}{2}\mathrm{H_2g} + \tfrac{1}{2}\mathrm{Br_2l} &= \mathrm{HBrg} && \Delta H^\circ_{298} = 8{\cdot}66 \text{ kg.-cal.}\\ \mathrm{Brg} &= \tfrac{1}{2}\mathrm{Br_2l} && 26{\cdot}71\\ \mathrm{H_g} &= \tfrac{1}{2}\mathrm{H_2g} && 52{\cdot}09 \end{aligned}$$

Thus $D(\mathrm{HBr})_{298} = 87{\cdot}46$ kg.-cal., corresponding to $D_0(\mathrm{HBr}) = 86{\cdot}60$ kg.-cal./mole.

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THE HYDROGEN BROMIDE MOLECULE ION, HBr^+

Early attempts[1] to excite a spectrum of hydrogen bromide were unsuccessful. Subsequently Norling[2,3] showed that a band-system of HBr^+ may be excited in hollow-cathode discharges through gaseous hydrogen bromide. The system, $^2\Sigma^+ - {}^2\Pi_i$, is entirely analogous to the system observed for HCl^+. Norling carried out rotational analyses of the 1,0 and 0,0 bands: the 0,1 and 1,1 bands have since been studied.[4] Constants for the two states are given below:-

State	T_0, cm.$^{-1}$	ω_e, cm.$^{-1}$	$x_e\omega_e$, cm.$^{-1}$	r_e, A.
A $^2\Sigma^+$	29227	1409	40	1·684
X $^2\Pi_{1/2}$	2653	2450	50	1·448
$^2\Pi_{3/2}$	0			

The value of the dissociation energy for the ground state may be obtained from the cycle:-

$$D_0(HBr^+) = D_0(HBr) + I.P.(Br) - I.P.(HBr).$$

With $D_0(HBr) = 86{\cdot}6_0$ kg.-cal., $I.P.(Br) = 11{\cdot}84$ eV., and $I.P.(HBr) = 12{\cdot}10$ eV.,[5,6] there is obtained $D_0(HBr^+) = 80{\cdot}6_0$ kg.-cal. Thus the molecule-ion is slightly less stable than the hydrogen bromide molecule.

Both the spin-splitting in $A\ ^2\Sigma^+$ and the Λ-doubling in $X\ ^2\Pi_i$ are large, and the system illustrates these effects particularly clearly.[6,7]

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BROMINE OXIDES

DIBROMINE MONOXIDE, Br_2O

Extinction coefficients of dibromine monoxide in carbon tetrachloride solutions containing free bromine have been measured[1] in the range 4000 to 7500 A. There is a shallow maximum at about 6400 A.: at 4000 A., $\epsilon(Br_2O) \sim 100$ which may be compared with $\epsilon(Br_2) \sim 200$.

Refs. p. 797

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BROMINE OXIDE, BrO

Emission bands in the region 4000 to 5000 A. have been observed in the spectra of various flames, e.g. that of ethyl bromide burning in oxygen[1] and in the oxygen-hydrogen flame to which methyl bromide or bromine has been added.[2] The bands are red-degraded, and their vibrational analysis supports the identification of the emitter as the molecule BrO. The constants (cm.$^{-1}$) are as follows:-[2]

State	T_0	ω_e	$x_e\omega_e$
A	24813	$\Delta G'_{1/2} = 457$	
X	0	713	7

It is not certain that the state X is the ground state of the molecule. The value of the energy of dissociation obtained by extrapolation is about 40 kg.-cal./mole.

Unlike ClO, BrO is not detected in the reaction between bromine and oxygen in flash photolysis.[3]

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THE BROMIDE ION, Br

The bromide ion dissolved in water does not absorb heavily in the near ultra-violet region of the spectrum.[1-5] The extinction coefficient, ϵ, attains a value of one at about 2300 A.: the absorption then rises rather steeply with decreasing wave-length to a maximum with $\epsilon = 1{\cdot}1 \times 10^4$ at 1995 A., followed by a second maximum[6] with $\epsilon = 1{\cdot}2 \times 10^4$ at 1900 A. The separation between these peaks is somewhat smaller than the separation $^2P_{1/2} - {}^2P_{3/2}$ in the bromine atom. Similar results are obtained with non-aqueous solvents: the effect of raising the temperature of the solution is to shift the absorption to somewhat longer wave-lengths.[5] The transition responsible for this spectrum is interpreted as a charge-transfer process[7,8] (see page 655).

Observations on the ultra-violet absorption spectra of solutions of bromine in aqueous potassium bromide provide evidence[9] for the existence of the tribromide ion, Br_3^-.

The effect of dissolved potassium bromide on the absorption band of water at 0·77 μ has been studied.[10]

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HYPOBROMOUS ACID, HBrO: THE HYPOBROMITE ION, BrO^-

Both these species absorb appreciably in the near ultra-violet region.[1] The value of the extinction coefficient, ϵ, for hypobromous acid is about 10 at 3850 A.: the absorption increases slowly with decreasing wave-length and has been followed to $\epsilon = 15$ at 2800 A.

The hypobromite ion shows a maximum ($\epsilon \sim 280$) at 3300 A., a minimum at about 2600 A., and a further increase in absorption towards shorter wave-lengths.

Reference

1 Farkas, L. & Klein, F. S., *J. Chem. Phys.*, 1948,**16**,886-93. (*42*,8087)

BROMIC ACID, $HBrO_3$

The Raman spectrum of a strong aqueous solution of bromic acid (50·6%) indicates that at this concentration the halogen is all in the form of bromate ions, BrO_3^-, of symmetry[1] C_{3v}.

Reference

1 Fonteyne, R., *Natuurw. Tijdschr.*, 1939,**21**,141-4. (*33*,6158)

THE BROMATE ION, BrO_3^-

The absorption spectrum of the bromate ion in the ultra-violet region has been measured.[1] The molar extinction coefficient, ϵ, increases from a value of about 1 at 2700 A. to about 2000 at 2000 A. (The chlorate ion has $\epsilon \sim 1$ at 2250 A.). The maximum lies at some undetermined wave-length below 2000 A. The spectrum is interpreted as a charge-transfer process (see page 655).

The Raman spectra of aqueous solutions of bromates have been studied by a number of workers.[2-6] The observation of four shifts, together with the results of depolarization measurements,[4] indicate that the ion, like the chlorate and iodate ions, is pyramidal, with symmetry C_{3v}. The assignments and degrees of depolarization, ρ, of Shen, Yao and Wu[4] are as follows:-

	Species	ν, cm^{-1}	ρ
ν_1	A_1	806	0·38
ν_2	A_1	421	-
ν_3	E	836	-
ν_4	E	356	0·89

Solutions of magnesium and zinc bromates in ethyl alcohol and in acetone have also been studied:[7] the changes in Raman frequency from the values in aqueous solution are very small.

The Raman spectra of crystalline bromates differ in important respects from the spectra observed in aqueous solution[3,5,8-10] although the bromate ion retains its C_{3v} symmetry in the crystal. However the frequencies of the ion are split in the crystal field[8] and the intensities and depolarization factors depend on the orientation of the symmetry axes of the crystal relative to the directions of irradiation and observation in ways not yet fully understood.[8,10]

The infra-red spectra of crystalline bromates have been studied both by reflection[11] and absorption.[12,13]

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SECTION XXVIII

THE ANALYTICAL DETERMINATION OF BROMINE, BROMIDE, HYPOBROMITE, AND BROMATE.

By L. A. HADDOCK

THE TITRIMETRIC DETERMINATION OF BROMIDES USING INDICATORS

THE reaction $Br^- + HCN + 2 + \rightarrow BrCN + H^+$ may be used for the determination of Br^-,[1] either by measuring the amount of oxidizing solution required, or by removing the excess of oxidizer and titrating the cyanogen bromide with thiosulphate after adding potassium iodide. Reducing agents such as acid solutions of arsenite, hydrazine, CNS^-, oxalate, nitrite and Fe^{++} do not reduce cyanogen bromide but will reduce oxidizing agents such as potassium iodate.

The ions Br^-, Cl^- and I^- may be determined in presence of one another by a modification of this method.[2] To the sample dissolved in 50 ml. of water are added 10 ml. of N-potassium cyanide solution, enough hydrochloric acid to make the concentration 10% and potassium bromate solution added dropwise until the yellow colour of bromine is no longer evident. Immediately afterwards 20 ml. of 10% aniline hydrochloride solution and 10 ml. of approximately 0·1 N-potassium bromide are added and, after 30 sec. or longer, 1 g. of potassium iodide; the liberated iodine is then titrated with thiosulphate. The method has been used for the determination of bromide in oilfield water[3] and for the microtitration of Br^-.[4]

A number of adsorption indicators have been recommended for use in the argentometric titration of Br^-. Eosin or fluorescein gives better end-points with Br^- than the Mohr chromate end-point.[5] The use of diphenylamine blue has been proposed:[6] the hydrosol silver bromide adsorbs the indicator to give a green solution which becomes clear and violet at the end-point, and acidities up to 5N. can be tolerated. The general use of Fajans' indicators (eosin etc.) has been reviewed and the effects of cations on the argentometric titration of Br^- predicted.[7] The use of α-naphthoflavone for Br^- has been suggested[8] and the use of copper nitrate with benzidine acetate has been recommended for Br^-, but not for Cl^-.[9] A range of luminescent indicators such as sodium fluorescein, erythrosin, phloxin, rhodamine 6G, primuline, thioflavine S, umbelliferone etc. are available,[10] with which titrations are carried out in ultra-violet light and under certain conditions one halogen may be determined in presence of another. Mixed absorption indicators have been proposed, e.g., fluorescein and methylene green for Br^- in neutral solution.[11] If excess of 0·01N-silver nitrate is added to the neutral Br^- solution containing one drop of *p*-ethoxychrysoidine solution, and the silver bromide is coagulated, the excess Ag^+ can be titrated with 0·01N-potassium iodide solution. The colour change produced is from red to yellow, while the precipitate at the end-point is deep red.[12] N-Methyldiphenylamine red in a strongly acid solution has been used as an absorption indicator[13] while some workers prefer resorcinolquinolein and resorcinolcinchomeronein as indicators in the titration of Br^- against Ag^+ in presence of acetic acid.[14]

Numerous proposals have been made to use Hg^+ or Hg^{++} in place of Ag^+ for the titration of Br^- and excellent results are obtained by using mercurous nitrate in the presence of sodium alizarinsulphonate as adsorption indicator.[15] Bromophenol blue may be similarly used[16] as also may chlorophenol red and bromocresol green.[17] If 0·1 ml. of 1% diphenylcarbazone is used as indicator, Br^- may be titrated with mercuric nitrate in a solution which is 0·2N. in acidity with nitric acid.[18] Mercurous perchlorate may be used with bromophenol blue as adsorption indicator,[19] while mercuric nitrate may be used with diphenylcarbazide in the presence of about 10/-/15% of dioxan added to the aqueous solution.[20] Other workers also recommend mercuric nitrate, but use as indicator 1 g. of mercuric chloride and 0·5 g. of diphenylcarbazone in 100 ml. of acetone;[21] ether is added to prevent interference by adsorption as the reaction depends upon a Hg^+/Hg^{++} balance. Tetraiodophenolsulphophthalein has been employed as indicator;[22] it helps to coagulate the mercurous bromide in acid solution, and imparts to it a pale yellow colour which at the end-point changes to violet.

Oxidation of Br^- to bromine, followed by distillation of the latter, is widely recommended. A modified Lange apparatus for this determination is described.[23] The bromine is libetated with potassium permanganate and dilute sulphuric acid and subsequenrly absorbed on zinc dust to form zinc bromide. This method which is much used in the potash industry is further described by other workers.[24] Alternatively, the bromine thus distilled off may be caught in sodium bisulphite solution, the excess sulphur dioxide removed by blowing air through the solution after acidification, and the bromine again liberated with standard potassium permanganate solution and measured by the volume of oxidizing agent used.[25] Among other oxidants proposed are chromic oxide[26] and chloramine-T;[27] with the latter in acid solution some bromine is liberated while $MeC_6H_4SO_2NBr_2$ is also precipitated.[28]

In a concentrated solution containing HCO_3^-, bromine can be converted into BrO_3^- by means of an excess of chlorine, and after removing this excess with phenol the BrO_3^- can be reduced in sulphuric acid solution by adding I^- and the liberated iodine then titrated.[29] 10 ml. of N-potassium hypochlorite in 0·1N-caustic potash may be used for this oxidation. The mixture is heated to 85°C. and saturated boric acid solution is added. After 5 minutes further heating excess hypochlorite is destroyed by means of N-hydrogen peroxide. Excess of this latter is itself destroyed by boiling.[30] The following simple method may also be used for the determination of Br^-. Precipitate Br^- as silver bromide by means of a measured volume of 0·1N-silver nitrate. Filter off the precipitate and wash it well. Add starch and 0·1 ml. of 0·1N-Ce^{++++} solution. Titrate the mixture with 0·1N-potassium iodide to a permanent blue colour.[31]

THE VOLUMETRIC ESTIMATION OF BROMIDES ELECTROMETRICALLY

Bromine may be determined electrometrically by direct titration in hydrogen cyanide solution, using a monometallic electrode system, with potassium permanganate to form cyanogen bromide; I^- is also oxidized to cyanogen iodide but a selective determination of I^- is possible so that Br^- may be determined rapidly in presence of considerable Cl^- or I^-.[32] A potentiometric method for the titration of bromide with silver nitrate is carried out with two silver wire electrodes connected through a galvanometer; one wire is kept immersed in the stirred solution while the other, wound on an absorbent non-conducting rod, is withdrawn during the titration.[33] The potentiometric titration of free bromine with titanous chloride has been proposed,[34] but it is said that hydrazine is better than titanous chloride because of its greater stability.[35] Free bromine liberated from BrO_3^- may be titrated with thiosulphate solution, using a platinum electrode and a calomel cell.[36] Bromine in brine is measured by potentiometric titration with hypochlorous acid in the presence of sulphuric acid and excess sodium chloride.[37] The following cell is described for the titration of Br^-:

$$Pt/Hg,Pb/PbSO_4/MgSO_4/unknown/AgBr/Ag.$$

The lead is present as a 5% amalgam.[38] Hypochlorite acidified with sulphuric acid may be used to oxidize Br^- in saline solutions. The mixture of chlorine and bromine is titrated with thiosulphate by a noncompensation measurement of the p.d. between the electrodes. After a short time of stirring (0·5 – 1 min.), the galvanometer reading is taken, the standard solution is added drop by drop until the galvanometer is deflected to 1 scale division, the reading is taken again and the amount of reagent added between the first and second readings is measured. The reagent is again added until the galvanometer is deflected to the next scale division and the procedure is repeated until the titration curve is completed.[39] By direct electrolysis of silver bromide dissolved in 20% potassium cyanide solution, using a rotating iron anode and a nickel-plated copper cathode, the error of a determination is less than 0·2%.[40]

A detailed study of the electrometric titration of halides in the presence of each other has been made.[41] In place of a silver electrode used in conjunction with a calomel cell, it is satisfactory to use a bimetallic electrode of mercury/silver and pure silver. Correct end-points for Br^- in presence of Cl^- may be obtained by adding 5% barium or sodium nitrate. It has been remarked that in potentionetric micro titrations, e.g. with 0·001N-potassium bromate, the change in direction of the precipitation curve does not correspond exactly with the end-point, and that the error is proportional to the volume of solution and to the solubility product of the precipitate and inversely proportional to the square of the normality of the solution.[42]

Free bromine may be titrated with 0·01N-aniline at pH 1·4 – 2·2, the end-point being reached at 830 mv.; the rheostat is then set for 966 mv. (18°C.), the direction of the current is changed and the Br^- is titrated with 0·01N-sodium hypochlorite after the addition of 5 ml. 20% sulphuric acid and 20 g. sodium chloride.[43] A rotating micro-electrode has been described for voltammetric measurements and current–voltage curves are given for bromine.[44] Silver bromide and silver iodide do not cathodically depolarize a rotating platinum electrode, but silver chloride causes a cathodic current to pass even in presence of excess Cl^-.[45] It is possible therefore to titrate Br^- or I^- in presence of Cl^- if no gelatin is added to suppress the current due to silver chloride. By this method Br^- may be determined to within 1% in 0·02 – 0·1N-Br^- solution, but the results are inaccurate in more dilute solutions.[46] Halide solutions may be electrolyzed with a silver anode at carefully controlled potential: the quantity of electricity used, as determined by a coulometer, is a measure of the amount of halide present. Mixtures of iodine and bromine (but not of bromine and chlorine) can also be determined with a high degree of accuracy by successive electrolyses at the appropriate potentials.[47]

THE DETECTION AND ESTIMATION OF BROMIDE IN PRESENCE OF OTHER INTERFERING RADICLES.

Bromide may be detected in presence of chloride by adding 1 ml. of 0·5% potassium permanganate and 1 ml. of phosphoric acid to 5 ml. of water containing 0·5 g. salt, and heating for some minutes in a tube covered at the open end with fluorescein paper: 0·2 mg. Br^- can thus be detected.[48] One part of Br^- in 40000 of Cl^- may be detected by a similar test, fluorescein being converted into the red dye eosin.[49] To detect bromide in sodium chloride (down to 3 mg. Br^- in 100 g.) 10 ml. of the solution is treated with 1 drop of saturated fuchsin solution (0·2%) and then a dilute chlorine solution (0·00024 g. Cl/ml.) using twice the number of drops previously found to decolorize 1 drop of the fuchsin in 10 ml. of water. If Br^- is present, a pink to violet coloration is observed.[50] This technique is a modification of Guareschi's test which is recommended.[51] If the solution is oxidized with 4 – 5% potassium permanganate or 10% chromic acid and the liberated bromine absorbed in weak potassium iodide solution, it is possible to detect 0·5 mg. of bromine in the presence of 1 g. of potassium iodide.[52] Potassium iodate and dilute sulphuric acid may be used to liberate bromine in presence of Cl^-.[53] If iodine is liberated from solution with sulphuric acid and hydrogen peroxide and adsorbed on charcoal, Br^- may then be detected in the filtrate.[54] Sodium perborate is also used as an oxidant for this purpose.[55]

To detect Br^- or Cl^- in presence of CNS^- 8 – 10 drops of pyridine and excess of neutral copper sulphate solution are added to a neutral solution of the salt: CNS^- is precipitated entirely as $Cu(C_5H_5N)_2(CNS)_2$, leaving Br^- in solution.[56] Similarly a nickel compound, $Ni(C_5H_5N)_4(CNSe)_2$ is used to remove $CNSe^-$.[57] The use of ammoniacal silver chloride solution to precipitate silver bromide is criticized because of its lack of sensitivity, and it is suggested that excess ammonia be replaced by hexamethylenetetramine.[58] The recommended procedure is as follows: dissolve 0·1 mol. of freshly precipitated silver chloride in a mixture of 300 ml. of cold saturated hexamethylenetetramine solution, 300 ml. of cold saturated sodium chloride solution and enough ammonia to maintain solution; add sufficient water to bring the total volume up to 1 litre. With 1 ml. of test solution and 1 drop of reagent, 0·01% bromine can be detected in Cl^- solution. The interference of CN^- during the titration of Br^- may be prevented by previously adding 5 ml. of 20% formaldehyde, whereby hydrogen cyanide is converted to glycollate and hexamethylenetetramine.[59] A comprehensive scheme for detecting CNS^-, I^-, Br^- and Cl^- in a mixture has been described.[60]

To determine Br^- in presence of excess I^- the latter is liberated by means of sodium nitrite and sulphuric acid and removed by filtration, followed by boiling, when Br^- (and Cl^-) remain in solution.[61] Sulphuric acid, sodium nitrite and chloroform may be used to remove I^- from solution,[62] Br^- being simultaneously oxidized to BrO_3^-.[63] Iodine as hydrogen iodide may also be removed by means of acetone, $2HI + HIO_3 + 3C_3H_6O \rightarrow 3C_3H_5IO + 3H_2O$: neither hydrogen bromide nor chloride is thus oxidized and they may be determined argentometrically.[64]

Bromine may be liberated quantitatively from a solution containing some hydrogen chloride by means of acid hydrogen peroxide:[65] the bromine is distilled off and absorbed in brine or magnesia, or alternatively it may be extracted with petroleum spirit.[66]

If permanganate is used as oxidant, bromine and chlorine are liberated from Br^- and Cl^- while I^- is oxidized to IO_3^-.[67] Potassium permanganate with phosphoric acid has been recommended[68] and it is said that I^- will oxidize mainly to IO_3^- if sufficient permanganate is present, but there is a tendency for chlorine to be liberated if Cl^- is in high concentration. Dichromate may not be substituted for permanganate, as the former liberates chlorine much more readily.[69] If iodine is first removed with nitrite and acid, bromine may be distilled off after adding 3 g. of fresh manganese dioxide and 25 ml. of 20% sulphuric acid; the distillate is caught in 3% caustic soda containing some sodium sulphite.[70]

In the presence of Cl^-, bromide ion may be oxidized with acid potassium iodate to bromine, but very high concentrations of Cl^- interfere.[71] If I^- is present, some workers prefer to use periodate.[72] This reagent oxidizes I^- to IO_3^- in presence of boric acid while Br^- is oxidised to bromine, which must be continuously removed by air blowing. A mixture of nitric and chromic acids has also been recommended for the oxidation.[73] The determination of Br^- in presence of 1000 times as much Cl^- has been studied.[74] The two oxidation potentials are too close to permit a complete separation by selective oxidation, but it is possible to oxidize Br^- completely to bromine with very little oxidation of Cl^- to chlorine. If the liberated bromine is fixed as Br^- and the process repeated, a very good separation may be achieved. A buffered solution of fluorescein is used for determining losses of Br^- in Cl^- (0·1 μg. Br^- in 1 g. potassium chloride) and it is possible to distinguish between 0·1, 0·2, 0·4 μg. etc., of Br^- in the control tests. A study has been made of the errors in the potentiometric titration of Br^- and Cl^- in admixture caused by adsorption and the formation of a solid solution of silver chloride in silver bromide.[75]

Bromine may be titrated potentiometrically after it has been liberated by hypochlorous acid in the presence of excess potassium chloride.[76] The method may be applied also to a mixture of Br^- and I^-, but it is considered that hypochlorite oxidizes these ions to iodine monochloride and bromine monochloride.[77] Sodium hypochlorite may be used in presence of calcium carbonate to oxidize Br^- to BrO_3^-: excess OCl^- is then destroyed with sodium formate.[78] A controlled pH of 9·0 – 9·4 has been proposed for the oxidation of Br^- with a known amount of ClO^-. The BrO^- which is formed is reduced with alkaline phenol solution and excess ClO^- is then determined by arsenite titration. The recorded errors are less that 0·03 mg. on 20 – 100 mg. of bromine.[79]

It is possible to co-precipitate silver chloride and silver bromide on a micro scale, to weigh the precipitate and to convert it entirely into silver bromide by heating twice with 6 times its weight of ammonium bromide. Similarly silver bromide may be converted into silver iodide by heating with ammonium iodide.[80] This procedure has been endorsed provided I^- is removed by treatment with sulphuric acid, potassium iodate and acetone whereby iodine is converted into iodoacetone and so is not precipitated with silver nitrate.[81]

It is shown that even traces of Br^- in the potassium chloride of a calomel cell influence the e.m.f. and this phenomenon may be used as a means of estimating Br^- in potassium chloride.[82]

THE DETERMINATION OF BROMINE IN ORGANIC COMPOUNDS

The determination of bromine in organic compounds involves initially the methods already described for chlorine. After destruction of the organic matter, the evolved gases are absorbed by some suitable absorbent and the bromine is determined by one of the procedures previously described. If chlorine and iodine are present, a suitable method which allows the determination of bromide in the presence of iodide and chloride must be used, as outlined in the preceding paragraphs.

A number of errors may arise in determining bromine in heavily brominated bodies such as hexabromobenzene by Stepanov's method (sodium and alcohol). Good results may be obtained in such cases by replacing ethanol with butanol.[83]

Where it is desired to know only the bromine and not the chlorine content, and assuming that iodine is absent, a method such as the following may be used.[84] The sample is oxidized over a platinum catalyst and the halogens are absorbed in caustic soda solution: Br^- is then oxidized by hypochlorite to BrO_3^- which is titrated iodometrically. Other workers have also recommended this procedure[85] but some prefer to destroy organic matter in a Carius tube, which is subsequently opened at −75°C. in the presence of excess caustic soda solution.[86]

THE ANALYSIS OF HYPOBROMITES

Hypobromous and bromic acids may be determined together iodometrically. The former is destroyed by adding excess of phenol, while bromic acid remains unchanged and may be determined separately.[87] This procedure is recommended and it is noted that hypoiodous acid, but not iodic acid, reacts similarly with phenol.[88] For the determination of hypochlorous and hypobromous acids when present together, the total ClO^- and BrO^- is measured in bicarbonate solution by titration with arsenite, while ClO^- is determined by making the solution slightly basic with caustic soda, adding 0·5% phenol solution followed by a slight excess of caustic soda, and after shaking for 7 – 10 sec., adding first excess 0·1N-arsenite solution and 75 ml. of 5% sodium bicarbonate, then 2N-acetic acid until effervescence occurs on shaking, and finally titrating with 0·1N-iodine. Further modifications allow the simultaneous determination of Br^-, Cl^-, ClO_3^- and BrO_3^-.[89]

THE ANALYSIS OF BROMATES

Bromates, like chlorates, may be measured by the quantity of reducing agent required to reduce a known quantity of the salt. For this reason most of the methods embodying this principle and described under chlorine may be employed. The optimum conditions for the electrolytic reduction of BrO_3^- in 0·5N-hydrochloric or sulphuric acids have been described.[90] A mixture of bromine, Br^- and BrO_3^- in neutral solution may be analysed as follows. Bromine is titrated potentiometrically against 0·01N-aniline sulphate, after setting the instrument to 830 mV.: the poles are then reversed and set at 800 mV., and an excess of 0·01N-antimony trichloride, 20 g. sodium chloride and 5 ml. of 20% sulphuric acid are added, the excess Sb^{+++} being titrated with 0·01N-$KBrO_3$. Finally the bromine now present in solution is titrated with 0·01N-hypochlorite.[91] Bromate, hypobromite and bromide in admixture may be analysed by the methods used for the corresponding chlorine compounds, the main difference being that Br^- in acid solution is quantitatively oxidized to BrO^- by means of BrO_3^-.[92] Methods depending upon the determination of free halogen by expelling it in a stream of gas do not give good results with bromine.

Fourteen µg. of potassium bromate may be detected in 2 ml. of solution by adding 1 ml. of 3 – 4N-hydrochloric acid and 1 – 2 drops of 0·015% methyl orange solution: ClO_3^-, IO_3^-, $S_2O_8^-$ and other oxidizing agents react only after several minutes.[93] If 0·1 ml. of a solution of fluorescein is added to 1 ml. of test solution and the mixture is boiled, cooled and treated with 1 – 3 drops of 0·1M-chloramine, 10 µg. of potassium bromate can be detected in 0·2 g. of potassium chlorate.[94] Bromate and persulphate may be determined in admixture by means of the reaction of persulphates with potassium iodide in neutral solution whereby iodine is liberated; after acidifying with hydrochloric acid and adding ammonium molybdate as catalyst, BrO_3^- may then be determined and the results are good over the range 0·5 – 10 mg.[95] In the absence of Br^-, which must be removed if necessary, one drop of solution containing 0·4 mg. BrO_3^- reacts with a 0·5% solution of manganese sulphate in 50% sulphuric acid to give the coloured permanganate ion.[96] This reaction is not given by ClO_3^- or IO_3^-. The accuracy of Junck's method for the determination of BrO_3^- in presence of ClO_3^-, which depends upon the fact that BrO_3^- reacts with potassium iodide in dilute hydrochloric acid whereas ClO_3^- does not, is reaffirmed.[97] Some, however, criticize the reaction and maintain that potassium chlorate behaves similarly by a partial liberation of chlorine.[98] Others consider the test to be accurate and remark that all chlorates may contain up to 0·03% BrO_3^-; they suggest the use of phosphoric acid in place of hydrochloric acid.[99] This method has been used successfully in an investigation of various BrO_3^-–ClO_3^-–H_2O systems.[100]

A mixture of BrO_3^- and IO_3^- in solution has also been analysed by a similar method.[101] It is found that in the presence of potassium fluoride and very weak hydrochloric acid only IO_3^- reacts with potassium iodide; when the acidity is increased, BrO_3^- also reacts. The use of phosphoric acid, with sodium pyrophosphate if necessary, is proposed to overcome the interference of iron in the estimation of BrO_3^-.[102] Bromate solutions are reasonably stable in presence of acid unless this be sulphuric or phosphoric acid.[103] In further studies it was found that BrO_3^- decomposed slightly in hot sulphuric or nitric acid solutions. The use of BrO_3^- to oxidize small quantities of Br^- is not recommended.[104]

THE DETECTION AND DETERMINATION OF TRACES OF BROMINE

A reagent which has frequently been proposed for the detection of Br is fuchsin-sulphurous acid. To avoid confusing a positive reaction with a similar reaction for aldehydes, all excess sulphur dioxide should be removed, leaving in solution fuchsinleucosulphonic acid. The full reaction of this acid with bromine requires 14 atoms of bromine per mol.[105] If the test is used with chloroform, a blue colour in the chloroform layer is obtained with quantities of bromine less than 0·1 mg.[106] This test, also known as the Denigés-Chelle test, can be modified by using it as a spot test on porcelain, whereby 0·8 μg. bromine may be detected.[107] Iodine interferes, though F^- or Cl^- does not; the ions S^{--}, SCN^-, SO_3^{--}, and $S_2O_3^{--}$ are destroyed by prior treatment with perchloric acid.

The reaction of bromine with fluorescein, or better ethylfluorescein, to yield the red dye eosin has been described by many workers. A method of preparing test papers has been described, and it is found that when bromine is liberated with acid permanganate, 0·001% Br^- in sodium chloride may be detected.[108] If chlorine is used to liberate the bromine, an excess of chlorine will bleach the eosin colour.[109] Nitrous and nitric acids interfere and must be removed by reduction with zinc.[110] If hydrogen peroxide and nitrous acid are used to liberate bromine, the reaction is sensitive to 1 part in 12500.[111] The eosin stain is more easily visible in ultraviolet light.[112] Iodine reacts similarly with fluorescein. The red colour produced by bromine is unstable in bright light.[113] One μg. of Br^- in chloride can be detected by liberating it with lead peroxide and boiling dilute acetic acid, the chloride being unattacked.[114]

Bromine dissolved in dry carbon tetrachloride may be detected by adding a solution of 0·3 mg. of dithizone in 100 ml. carbon tetrachloride: the colour change is to intense red and the reaction is very sensitive.[115] Bromine is separated from Cl^- by the action of hydrogen peroxide and sulphuric acid and is taken up in a layer of carbon tetrachloride; if iodine is present, sodium nitrite is added to the solution before separating the bromine from Cl^-.

Bromide and iodide, but not chloride, give colorations when heated with strychnine and potassium persulphate in dilute phosphoric acid solution.[116] The characteristic crystals produced by as little as 0·5 μg./ml. of bromine when it reacts with *m*-phenylenediamine have been described; chlorine and iodine do not interfere with the test.[117]

The Guareschi fuchsin test is used quantitatively to determine traces of bromine in organic matter, the bromine being liberated by acid permanganate.[118] This technique is also satisfactory for the determination of bromine in blood.[119] If 10 ml. of Folin-Wu blood filtrate are added to 30 mg. potassium permanganate and 3 – 4 drops of sulphuric acid followed by 1 ml. of fuchsin reagent (5 ml. of concentrated hydrochloric acid and 500 ml. 0·01% aqueous fuchsin solution decolorized with 5 ml. saturated solution of sodium bisulphite), the mixture becomes violet and then pink.[120] One drop of sodium bisulphite solution is added to restore the violet colour and after clearing the solution with fuller's earth, the solution is extracted with 5 ml. of acetone and compared with prepared standards. The presence of iodine interferes with the method.

The fluorescein-eosin conversion has been extensively employed in a quantitative manner. This reaction enables Br in body tissues to be determined. After the tissues have been ashed the bromine is liberated by means of chloramine-T. The error on solutions containing 0·4 to 3·5 μg. bromine is less than 0·1 μg.[121,122] To test the purity of the high grade chlorides required for the preparation of standard cells, the fluorescein test for Br^- may be modified by the use of uranin, whereby 0·001 mol.% bromine may be detected.[123]

Phenol red (colour change yellow to red at pH 6·4 – 8) reacts with BrO^- to form an indicator of the bromophenol blue type (yellow to blue at pH 3·2–4·6). The oxidation of Br^- and the bromination of phenol red is effected by using calcium hypochlorite in a borax buffer at pH 8·7 – 8·8: the final colour comparison is made at pH 5·0 –5·4, and 1·4 μg. Br^-/ml. may be determined.[124] The conversion of rosaniline to red-purple pentabromorosaniline has been used as the basis of a colorimetric method for 50 – 400 μg. of bromine.[125]

Bromine in foodstuffs may be estimated by oxidizing the material with sodium peroxide and then oxidizing the Br^- to BrO_3^- by means of hypochlorite in the presence of sodium dihydrogen phosphate. Excess of hypochlorite is destroyed by boiling with sodium formate and the BrO_3^- produced is measured by adding potassium iodide to the acid solution and titrating the liberated iodine.[126,127]

Over 150 papers published on the microdetermination of bromine have been listed by Leipert.[128]

THE DETERMINATION OF BROMINE IN WATER AND BRINE

The Br^- content of saline water may be measured by liberating bromine with potassium permanganate and phosphoric acid. The liberated bromine is allowed to react with a specially prepared fuchsin solution and the intensity of the colour produced is measured after it has been concentrated in chloroform. Any iodine present is removed by prior treatment with sodium nitrite, dilute sulphuric acid and chloroform.[129] A detailed study has been made of the liberation of bromine from very saline solutions by oxidation with permanganate at controlled acidity.[130]

Weszelszky's original procedure has been modified.[131] Iodine is removed with carbon disulphide after the addition of sodium nitrite and acid, the Br^- being then oxidized to potassium bromate by means of potassium hypochlorite. Unlike potassium chlorate the bromate reacts with hydriodic acid. The suitability of the volumetric method of d'Ans and Höfer, based upon the oxidation of Br^- to BrO_3^- with hypochlorite, has been confirmed[132] but some alterations are made in the concentrations of the reagents. Other workers consider the method of d'Ans and Höfer slightly superior to the colorimetric phenol-red procedure of Stenger and Kolthoff and use it successfully to determine 0·03 – 2·3 p.p.m. Br^- in well waters.[133] The oxidation of Br^- to BrO_3^- by means of boiling dilute hypochlorite solution at pH 6·0 – 6·5 has been further recommended.[134] Excess hypochlorite is destroyed by adding sodium formate to the hot solution. Any iodide present is also oxidized under these conditions to iodate. The sodium bromide content of table salt has been measured in this manner except that chlorine water was substituted for hypochlorite and the solution was buffered with boric acid.[135] The average bromine content of table salt was found to be 0·02%.

A comprehensive survey of the Br^- content both of sea water and of Cheshire brines has been made,[136] and the authors recommend the procedure of Kolthoff and Yutzy.[132] The solution to be tested is neutralized to methyl red, buffered with sodium dihydrogen phosphate and treated with sodium hypochlorite. The mixture is then boiled, treated with sodium formate, cooled and titrated with thiosulphate after adding potassium iodide, dilute sulphuric acid and a drop of ammonium molybdate. The oxidation of Br^- to BrO_3^- takes place completely between pH 4.12 – 7.35. Under the same conditions, I^- is also oxidized to IO_3^- and allowance must be made if it is present. Other workers prefer to oxidize Br^- at pH 6 – 7: they point out that BrO_3^- is reduced by formic acid in hot dilute sulphuric acid, but that IO_3^- is not affected and suggest this fact as a means of determining IO_3^- in the presence of BrO_3^-.[137]

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THE DETERMINATION OF BROMINE AND BROMINATED COMPOUNDS IN THE ATMOSPHERE

Most of the methods proposed for the detection and determination of chlorine in the atmosphere can equally well be applied to bromine and to brominated compounds. This generalization applies particularly to the use of the copper halide lamp and to reactions involving the oxidation of a selected organic compound to form a coloured product. The reaction of resorufin with bromine to form tetrabromoresorufin has been proposed as a method for determining the halogen. The disappearance of the characteristic fluorescence of resorufin after bromination may be used as a test for bromine.[138] Bromine (or chlorine) is detected in air by passing it through a 10% alcoholic solution of pyramidone. A violet colour is produced in the presence of the halogens, but the test is slightly less sensitive than that given by starch-iodide paper.[139]

The amount of iodine and bromine vapour in admixture in the atmosphere is also determined by absorbing the vapours in 0.02N-caustic potash, evaporating the resulting solution to dryness and carefully igniting the residue to destroy organic matter. The resulting I^- and Br^- are determined together by oxidation with OCl^- in a buffered solution. Another half of the original solution is treated with a small amount of chlorine to oxidize iodine to IO_3^-, excess chlorine is boiled off and sodium formate is added, after which IO_3^- is determined iodometrically. The difference between the two determinations gives the amount of bromine in the air.[140] Bromine may also be absorbed on activated charcoal which is subsequently oxidized: the liberated bromine is then made to react on a small area of fluorescein paper.[141]

Traces of volatile bromides such as ethyl bromide may be determined in air by passing the air together with some water vapour through a heated quartz tube.[142] The hydrogen bromide produced is condensed with water after passing through a condenser and the Br^- is determined colorimetrically.

Other workers have passed the air through a pyrolysis chamber and thence around a transparent indicating film. Light passing through this film to a photocell activates a signalling device, which responds within two minutes to 0.004 mg./l. of bromine.

PHYSICAL METHODS FOR THE DETERMINATION OF BROMINE

Several workers have proposed the use of monochromatic *X*-rays, whereby bromine may be determined, for instance, in a mixture of potassium iodide and potassium bromide, with an error of less than 1%.[144] A 'light spectrograph with curved crystals' may be used for the measurements.[145] The application of *X*-ray spectral analysis to elements from magnesium to uranium has been reviewed.[146]

A hot arc source is described for the spectrographic determination of halogens giving high levels of ionization and excitation, and working curves are given for bromine.[147] Bromine may be measured in aqueous solution using a copper electrode and an a.c. arc with a large capacity shunt in a circuit with low self-inductance.[148] By using the lines 4704, 4785, 5332, bromine may be detected at a concentration of 0·001%.[149] A solution containing Br^- may be allowed to drip into an a.c. arc through an opening in a copper tip used as the lower electrode: by using the line 4785·5 it is possible to determine 0·001% Br^- and with the lines 4678·7 and 4816·7 to determine 0·01% Br^-.[150] The conditions most favourable for the determination of bromine are described. The most sensitive lines for use are 2389·7 and 2926·3.[151] The extinction coefficients of Br^- in aqueous solution at $2 = 463\mu\mu$ have been measured and the technique is applied to the analysis of aqueous solutions of bromides.[152] A general review on the photometric determination of bromides has been published.[153]

The polarographic determination of bromate together with chlorate and iodate is described:[154] bromide ion may be oxidized to BrO_3^- with hypochlorite prior to its polarographic determination.[155] Both IO_3^- and BrO_3^- can be determined in admixture because of the considerable difference between their reduction potentials, while Cl^-, ClO_3^- and ClO_4^- are not reduced at the cathode even at concentrations of $10^6 : 1$ and do not, therefore, interfere with the determination.

The use of ion exchange materials has been suggested for the separation of Br^- and I^-. A procedure has been given for the separation of chloride group anions by partition chromatography on paper using as solvent butanol saturated with 1·5N-ammonia.[156] Subsequently the paper is sprayed with 0·1N-silver nitrate, washed twice with dilute nitric acid to remove excess silver and then held over hydrogen sulphide. Chloride produces a brown spot (*Rf* 0·10 – 0·11) and bromide a brown spot (*Rf* 0·15 – 0·18), *Rf* being the ratio of the distance travelled by the ion to the distance travelled by the liquid front.

Neutron bombardment may be used for the estimation of small quantities of bromide as the induced activity of bromine may be measured after 4 hours, whereas the half-lives of active chlorine and iodine are much shorter, 35 min. and 25 min. respectively.[157]

THE ANALYSIS OF LIQUID BROMINE

The determination of water in liquid bromine has been carried out by vaporising the sample and passing the gas through phosphorus pentoxide tubes.[158] Bromine saturated with water contains 0·05%. Iodine can be determined in bromine by dissolving the sample in 25% potassium bromide solution and destroying the bromine in an aliquot portion by means of sodium formate: any free iodine remaining is titrated with sodium thiosulphate.[159] Free chlorine may be determined by means of the greatly diminished solubility of bromine in concentrated potassium bromide solution in presence of potassium chloride. The change is measured volumetrically and good results are obtained over the range 0 – 1·2% chlorine.[160] Three methods for determining chlorine in liquid bromine have been studied critically.[161] The density method of Kubierschky was found to be reasonably accurate and rapid. The cryoscopic method was less reliable, but the results were within 0·5% of the true value: a study of the freezing point of liquid bromine indicates that 0·4% chlorine lowers the freezing point by about 1°C.[162] Other speedy and accurate methods for the chemical determination of chlorine in bromine have been proposed.[163]

The induction period of the olefine-bromine reaction has been suggested as a criterion of purity of bromine.[164]

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SECTION XXIX

BIOLOGICAL PROPERTIES OF BROMINE

By G. M. DYSON

It has been suggested that bromine is an essential element in animal life, but this is not proved[1] although the presence of bromine has been demonstrated in the alimentary economy of certain shell-fish (*Murex* and *Purpura* sp. contain 6,6-dibromoindigo[2] giving rise, in earlier times, to dyeing processes). Many communications have been published on the replacement of chloride ion by bromide ion in normal physiological processes, but the subject is outside the scope of this volume. In general the effect of bromine on plants has been but slightly examined; 30 p.p.m. of bromine exerts a stimulant effect on the germination of seeds, but greater quantities lead to some slight loss of germinating power; in general bromates depress germination much more than bromine or bromides.[3] Bromine has been shown to be a specific mutafacient in *Allium cepa.*[4] Dilute aqueous solutions of bromine exert considerable germicidal action;[5] less than 0·25 p.p.m. of free bromine in water kills *Staphylococcus aureus, S. albus, Escherichia coli,* and *Eberthella typhosa* in 15 – 30 sec. at room temperature, whilst yeast is killed by slightly higher concentrations. Mould spores require 5 – 30 p.p.m. and the spores of aërobic bacteria 40 – 220 p.p.m. at pH 3·5 – 4 and 100 – 450 p.p.m. at pH 6·8 to 7·2. Bromine is therefore intermediate between chlorine and iodine in its activity on bacterial spores,[6] and this order of activity also holds for the hypohalous acids. A more detailed examination by Wyss and Stockton[7] of the time required for a 99% kill of *B. subtilis* and *B. metiens* showed that the time is an exponential function of bromine concentration in buffered solutions and that the Br_2 molecule is the active agent. Gershenfeld and Witlin[8] showed that with certain organisms iodine at 1 in 5000 had a greater activity than either bromine or chlorine at that concentration, both at 24° and at 37°. From these observations have sprung recommendations that bromine in dilute aqueous solution be used for wound irrigation[9,10] and for the sterilization of potable water supplies.[11]

The use of bromine compounds in food preservation has been suggested, despite the fact that it would be contrary to English law. The use of bromate in canning[12] is covered by a British Patent, and several proprietary preservatives, based on 2-bromoethanol[13,14] have been described.

The use of ^{82}Br as a radioactive tracer in the solution of various physiological and biochemical problems has been widely applied and is described elsewhere (see page 1052). It has also been used to investigate the fate of bromate in baking.[15,16] Many flours supplied for breadmaking contain traces of bromates which have a pronounced action in maintaining the size of the loaf; this is attributed to its inhibiting action on certain proteolytic enzymes.

TOXICITY

Although bromine is known to be toxic if breathed as vapour, and to cause severe burns, there is little published data on this aspect of its activity.

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Rumpel[17] ascertained that fatal illness is to be expected after ½-1 hr. exposure to a bromine concentration of 0·05 mg./l. (= 0·0076 vol.-%); similar data have been recorded by Carboneschi.[18]

There is a voluminous literature on the effects of bromide poisoning, bromides have long been widely used as sedatives and it is stated that 2-3% of patients medicated with bromides show some toxic symptoms. It appears that when the concentration of bromide ion in the blood serum rises above 40-50 mg. per 100 c.c. toxic symptoms arise. These may be psychotic, dermal or in the form of a general intoxication. Fröshang[19] records that of 1582 patients having systematic bromide medication 46 had a blood-bromide content of 50 mg.-% and 5 had 246-480 mg.-%. The details of this subject are, of course, outside the scope of this treatise, but the methods of assay of small quantities of bromide in organic matter devised by Dalsgaard-Nielsen,[20] and based on the method of Hauptman[21] are of chemical interest. Likewise the work of Ishikawa,[22] which has demonstrated that bromide intoxication can be an allergic response to sensitization, and the observations of Cornbleet[23] on the acceleration of the elimination of bromide from the animal system by the administration of ammonium chloride deserve mention here.

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CHAPTER IV

IODINE

SECTION XXX

THE OCCURRENCE AND DISTRIBUTION OF IODINE

By G. J. HILLS

Iodine in the free state has not been detected in the lithosphere, except as small traces in certain mineral springs, but as iodide and iodate it occurs widely, although always in low concentration.[1-6] The following minerals contain iodine as an essential constituent, but with the exception of the last two, which form part of the Chilean saltpetre deposits, they are very rare.[7,8]

Coccinite	Hg_2I_2
Cuproiodargyrite	(Ag,Cu)I
Iodembolite	Ag(Br,I,Cl)
Iodobromite	2AgCl,2AgBr,AgI
Iodargyrite	AgI
Marshite	Cu_2I_2
Miersite	4AgI,CuI
Salesite	$CuIO_3OH$
Schwarzembergite	$Pb(I,Cl)_2,2PbO$
Tocornalite	(Ag,Hg)I
Dietzeite	$7Ca(IO_3),8CaCrO_4$
Lautarite	$Ca(IO_3)_2$

The evenness of distribution of iodine has been confirmed by numerous geochemical investigations and all igneous rocks and minerals have been found to contain it.[9,10] The iodine contents of some typical rocks and minerals are tabulated below:[7,11-16]

Rock	Iodine content (mg. per kg.)	Mineral	Iodine content (mg. per kg.)
Amphibolite	0·25 – 0·38	Apatite	0·23 – 0·44
Basalt	0·31 – 0·80	Biotite	0·50
Diabase	0·49 – 1·04	Calcite	0·23
Gneiss	0·38	Cinnabar	0·50
Granite	0·20 – 1·25	Cuprite	3·8 – 4000
Limestone	0·44	Dolomite	0·32
Marble	0·07 – 1·98	Fluorite	0·55
Mica schist	0·54	Gypsum	0·25 – 0·27
Porphyry	0·38 – 0·54	Limonite	0·75
Pumice	0·25	Pitchblende	0·94
Quartzite	1·10 – 3·70	Pyrite	0·20
		Serpentine	0·38
		Wulfenite	8·56

Phosphate rocks are usually rich in iodine, often containing up to 100 mg. per kg.; a sample from Limburg, Germany, contained as much as 280 mg. per kg.[7] Iodine is always present in iron and iron ore, the concentrations found varying from 0·10 to 1·10 mg. per kg.;[17] and since meteoric iron has also been found to contain from 0·14 to 1·50 mg. of iodine per kg., it is probable that iodine is present in the iron kernel of the earth.[9]

Many determinations of the iodine content of soils have been made and show that the amount present is usually between 0·2 and 12 mg. per kg. of dry soil, being greatest in heavy, clay soils and least in light, sandy soils.[7,18-32] The iodine in soils is believed to be of organic origin and the maximum concentration is found where there is also a high humus content.[33-35] As might be expected, therefore, coal is relatively rich in iodine, containing 0·85 to 11·17 mg. per kg.[36-39]

The concentration of iodides in secondary deposits has in general been precluded by their high solubility; well leached soils have a low iodine content and salt deposits are usually free from iodide.[40-46] The sole exception to this generalization is the Caliche beds in Chile, which contain from 0·02 to 1·00% of iodine mainly as iodate and remain the principal commercial source of iodine.[12,47-48]

The iodine content of many rivers and lakes has been determined and ranges from 0·00001 to 0·004 mg. of combined iodine per litre.[49-53] Subterranean waters are always richer in iodine, artesian well water, for example, containing up to 0·12 mg. per litre.[54-56] McClendon has tabulated in great detail the iodine contents of these and very many other sources of drinking water.[7] Natural spring waters are richer still in iodine,[7,57-62] those from Bad-Hall, Austria, containing iodides equivalent to 47 mg. of iodine per litre.[63-65] In many of these spring waters some elementary iodine is present. Natural brine wells also have a high iodide content and those at Salsomaggiore, Italy, containing the equivalent of 60·5 mg. of iodine per litre are utilized for the commercial production of iodine.[66] More recently, iodine has also been produced from the brine obtained from oil well drillings which may contain up to 144 mg. of combined iodine per litre.[7,8,67-75] Iodine, as iodide, is present in sea water, the average concentration being 0·02 mg. per litre, although there is much local and some seasonal variation.[7,76] In general, the concentration of iodine is approximately proportional to the salinity; in the Mediterranean Sea it is equivalent to 0·006 mg. and in the Baltic Sea to 0·001 mg. of iodide ion per litre.[7]

The existence of free iodine vapour in the atmosphere has not been confirmed but combined iodine in micro-organisms and dust particles is always present. The concentration of iodine is usually between 0·0005 and 0·002 mg. per cu. m.[77-79] but it varies greatly with locality and is greatest in the neighbourhood of spas[80,81] and the sea shore.[82-85] This is probably due to the presence of iodine-containing spray and sea winds are certainly much richer in iodine than land winds.[86] It has been calculated that up to 10,000 tons of iodine are discharged annually into the atmosphere by the combustion of coal,[36] although some of this iodine may be retained in soot which has been found to contain 49 mg. iodine per kg.[7] The iodine-containing particles in the atmosphere are rapidly removed by raindrops and the iodine content of the atmosphere is low during and after rainfall.[86]

The iodides and iodates in sea water enter into the metabolic cycle of most marine flora and fauna. The iodine content of many varieties of seaweed has been determined[87-103] (cf. Mellor II,18) and McClendon has tabulated the values obtained for several hundred species.[7] The variety *Laminaria* remains the most useful for the commercial production of iodine; the variation of its iodine content with depth below sea level, with locality and with the season has been studied in detail.[104] Keratinous sponges have been shown to contain from 0·12 to 1·21% of iodine and non-keratinous sponges 0·05 to 0·6%.[105-6] Although the protein constituent forms only a small part of the coral plant, it is rich in iodine, containing up to 9%.[107-8] The iodine contents of some marine molluscs, crustacea and fish are given below:[7,109-114]

Animal	Iodine content (mg. per kg.)	Animal	Iodine content (mg. per kg.)
Clam	2 – 6	Herring	0·9 – 1·0
Mussel	4 – 7	Mackerel	0·06 – 1·7
Oyster	0 8 – 6	Pilchard	0·3
Crab	0·8 – 6	Salmon	0·6 – 1·6
Lobster	0·6 – 11	Sardine	0·16 – 1·5
Cod	0·5 – 5	Sole	1·0
Haddock	1 – 24		

Fresh water fish have a much lower iodine content normally not exceeding 0·1 mg. per kg.[7]

The iodine content of meat is relatively small, averaging 0·02 mg. per kg.[7] Nevertheless, iodine is essential for normal mammalian growth and its concentration has been determined in most common food stuffs,[7,115-119] in drinking water[102-127] and in wine.[128-129] The iodine contents of some edible land plants are given in the following table:[7]

Material	Iodine content (mg. per kg.)	Material	Iodine content (mg. per kg.)
Grass	0·05 – 1·0	Grapes	0·007 – 0·120
Tea	0·07 – 0·83	Tomatoes	0·008 – 0·38
Oats	0·04	Beans	0·02 – 1·00
Wheat	0·03 – 0·06	Cabbage	0·15 – 0·29
Bread	0·002 – 0·10	Carrots	0·06 – 0·51
Apples	0·006 – 0·09	Lettuce	0·02 – 0·62
Bananas	0·005 – 0·03	Peas	0·05 – 0·08
Dates	0·005	Potatoes	0·01 – 0·20
Oranges	0·002 – 0·015	Spinach	0·10 – 0·70

The iodine content of any one type of plant, fruit or vegetable varies greatly with locality. In the above table, for example, the lower values almost invariably correspond to that species grown in New Zealand or Switzerland and the maximum values to products of the United States. Evidence has continued to accumulate showing the close relationship between the incidence of goitre and cretinism in human beings and a deficiency of iodine in their diet.[7,130-131]

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SECTION XXXI

THE PREPARATION AND MANUFACTURE OF IODINE

By G. J. HILLS

The fractional crystallization of Chile saltpetre and the subsequent extraction of iodine from the mother liquors is still the principal industrial method of producing iodine.[1,2] Numerous discussions of this method and its modifications and of related investigations have been published.[3-10] It has been shown, for example, that sulphur dioxide can be used successfully instead of sodium bisulphite[11] and that magnesium chloride in the liquors, by hydrolyzing to give hydrochloric acid, is responsible for the significant loss of iodine that sometimes occurs when the liquor is concentrated.[12] Most of the iodate, however, is still reduced by the addition of sodium bisulphite, and up to 1000 tons of iodine so obtained is exported annually from Chile.[2] Iodine may be obtained directly from crude saltpetre by heating it to 200 – 250°C. in a current of air, water vapour or sulphur dioxide.[13] The purified saltpetre still contains appreciable quantities of iodine and up to 0·024% has been detected; this is a valuable addition to its properties as a fertilizer.[15]

In spite of the economic advantages of the caliche process, the extraction of iodine from seaweed has continued in France, Japan and Russia, although only relatively small quantities are produced in this way.[16-18] The *Laminaria* rather than the *Fucus* variety of seaweed is usually collected because of its high iodine content,[1,19-21] (cf. Mellor, II, 18) although in Russia *Phyllophora rubens* is sometimes preferred,[22,23] as the ash is claimed to contain up to 1% of iodine.[24,25] Although it has been shown that low-temperature ashing of seaweed retains virtually all the iodine in the ash,[26] several attempts have been made to dispense with this costly stage of the process.[27-30] Most of the iodine in seaweed appears to be present as soluble inorganic salts and is easily washed out with water or dilute acid, leaving a residue valuable as a source of agar-agar and alginates.[28-30] The extraction of iodides from the raw weed is facilitated by continuous treatment with hot water[31] or by autoclaving.[32] The iodine may be recovered from the aqueous extract in various ways.

Treatment with chlorine,[33] nitric acid,[34,35] nitrous acid[36,37] or other oxidizing agents,[38] followed by distillation, filtration or solvent extraction of the iodine[37,39] is effective for concentrated liquors, but not for the aqueous seaweed extract which usually contains only 0·1% of iodine. The iodide may be concentrated by adding a soluble copper salt, sometimes with a reducing agent, when cuprous iodide is precipitated, filtered off and washed, the liquors being returned for further extraction. The cuprous iodide is then heated with sodium hydroxide at 350 – 375°C. to give sodium iodide from which iodine may be obtained.[40-43]

Attempts have been made to concentrate the iodine in dilute extracts by electrolysis and this method has also been applied directly to suspensions of seaweed.[44,45] Direct treatment of seaweed with sodium hypochlorite[46] or sodium bisulphite[47] has also been shown to liberate free iodine. Dry distillation of seaweed yields a tarry distillate containing most of the iodine.[48-50]

It has already been observed that many naturally occurring brines have a significant iodide content. Large quantities of brine become increasingly available as a by-product of the petroleum industry and the extraction of iodine from such brines has become an important source of this element and its salts, several hundred tons being produced annually.[2] Various extraction processes are used, all requiring a preliminary purification of the brine.[2,51,52] Sedimentation and filtration through sand remove oil and mud and the clear brine, which contains appreciable quantities of calcium and magnesium chlorides and bicarbonates, may be further purified from these salts by aeration,[53] by adding lime,[54,55] or by treatment with aluminium sulphate.[56]

In Java, the purified brine is allowed to percolate down a tower where it meets an upward stream of sulphur dioxide which liberates the iodine. The iodine suspension thus produced is then passed through reaction troughs containing bundles of copper wire in continuous agitation, whereby cuprous iodide is precipitated, and is then separated, washed and dried. This crude cuprous iodide, containing approximately 55% of iodine, is not further purified but is exported as such for use in the manufacture of iodides, iodine etc.[2,57]

In California, three methods of extracting iodine from brine are employed,[2,58] In the first, the purified liquors are acidified with sulphuric acid and sodium nitrite is added to liberate iodine. The yellow solution is then agitated with activated charcoal on which the iodine is adsorbed. The charcoal is used repeatedly with fresh iodine-containing solutions until it is nearly saturated and is then separated and leached out with a solution of caustic soda or sodium carbonate which finally contains approximately 3% of sodium iodide. This solution is treated with sodium dichromate in acid solution to give solid iodine which is filtered off.[2,59-64] Other oxidizing agents may be used to liberate the iodine, *e.g.* bleaching powder,[65-67] which has been shown to be the most effective,[67] chlorine,[68,69] ozone,[70,71] or oxides of nitrogen;[72-75] other adsorbing materials have also been investigated.[76-83] The adsorbed iodine may also be removed from the charcoal by treatment with steam, when the iodine distils off,[84] by treatment with ammonia to give ammonium iodide,[85] by treatment with sodium bisulphite to give a solution of hydriodic acid[86] or by electrolysis using the charcoal as a carbon cathode in an electrolysis cell.[87]

In the second Californian process, the purified brine is treated with chlorine gas and stripped of iodine by a countercurrent of air. The iodine is then absorbed in an aqueous solution of hydriodic and sulphuric acids into which sulphur dioxide is passed continuously. This solution, when sufficiently concentrated, is again chlorinated whereby the iodine is precipitated and then filtered off.[88-92]

The third method involves the addition to the filtered brine of an approximately 2% solution of silver nitrate in sufficient quantity to precipitate only the iodide ions. Efficient stirring ensures complete precipitation of the silver iodide almost free from contamination with silver chloride. A small quantity of ferric chloride is added to coagulate the precipitate which is filtered off, washed with concentrated hydrochloric acid to dissolve any ferric hydroxide and mixed with clean steel scrap. Metallic silver is rapidly formed together with ferrous iodide which passes into solution. The silver is filtered off for re-use and the filtrate treated with chlorine or other oxidizing agent to precipitate the iodine.[58,93] Alternatively the iodine may be recovered from the silver iodide by heating it with sulphuric acid to 270°C.,[94] by directly chlorinating it in suspension in carbon tetrachloride[95] or by treating it with aqua regia.[96]

In Russia also oil-well brine is used for the manufacture of iodine. The methods employed are similar to those used in California,[97-100] although the presence of naphthenic acids has sometimes necessitated special purification procedures.[101-103] Iodine, liberated by oxidation of the original filtered brine, is sometimes extracted with petroleum, carbon tetrachloride or other organic

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solvent:[104-106] it may also be recovered directly from the brine by electrolysis using silver or copper anodes which precipitate the insoluble metal iodides,[107-109] or carbon anodes which adsorb the liberated iodine.[110,111]

The Salsomaggiore mineral waters are treated with a mixture of sulphuric acid and sodium nitrite and the liberated iodine is extracted with petroleum and converted into sodium iodide by treating the hydrocarbon extract with sodium sulphite. Elementary iodine is then obtained by the usual oxidation of this concentrate with sulphuric acid and sodium dichromate.[112-114]

The crude iodine produced by any of these processes may be purified by melting it under concentrated sulphuric acid: practically all the impurities pass into the immiscible sulphuric acid layer which is run off after the system is cooled. The solid iodine is then broken up, washed free from acid and dried, and is then approximately 99·8% pure.[115-116] Alternatively, the iodine may be distilled with or without steam, condensed in 'udells' and dried. After either procedure, the iodine still contains small traces of impurities, the nature of which depends on the original extraction process. The main impurity in Chilean iodine is sulphur.[117] The iodine in waste iodide solutions may be recovered by chlorinating the solution and filtering off the liberated iodine which is then purified by steam distillation.[118] Several reviews of the iodine industry have been published[1,2,119-122] and, until recently, world production statistics were published annually.[123]

Colloidal iodine may be prepared by grinding ordinary crystalline iodine in a colloid-mill,[124] but a much more convenient method is to precipitate iodine chemically or electrolytically in the presence of a protective colloid such as gelatin.[125-128] The brick-red suspension is stable for several weeks and if sufficient dextrose or gum arabic is added, the solution may be evaporated to dryness, affording a solid which is redispersible in the colloidal state.[129] More recently, stable colloidal dispersions of iodine have been prepared by exposing aqueous suspensions of iodine to ultrasonic vibrations.[130] When solutions of the alkali iodides are subjected to these vibrations free iodine is liberated forming the tri-iodide ion.[131-133]

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SECTION XXXII

THE PHYSICAL AND CHEMICAL PROPERTIES OF IODINE

By G. J. HILLS

THE PHYSICAL PROPERTIES OF IODINE

The absorption of *X*-radiation by iodine has been studied[1-3] and its crystal structure has been determined.[4-6] Iodine crystallizes in the orthorhombic system and has a unit cell of 8 atoms arranged as a symmetrical bipyramid.[5] The cell constants at 18°C. in Angstrom units are a = 4·7761, b = 7·2501 and c = 9·7711.[6] There is no evidence of a monoclinic variety of iodine under ordinary conditions, although Bridgman has observed transitions to other modifications at very high pressures.[7] Data have been given for the construction of a model illustrating the arrangement of the atoms in solid iodine.[8,9] The amorphous structure of thin iodine films has been studied by electron transmission and reflection.[10] From the interatomic distances of a number of iodine-containing compounds the effective radius of the covalently bound iodine atom has been calculated,[11-13] the most recent value being 1·84 A.[14]

The vapour density of iodine has been redetermined over the temperature range 723 – 1274°K. and used to calculate the change in heat content and free energy for the dissociation of molecular iodine into atoms, $I_2 \rightleftharpoons 2I$, i.e., $\Delta H^\circ_{298\cdot1^\circ K.} = 36{,}057 \pm 50$ g.-cal.mole^{-1}; $\Delta G^\circ_{298\cdot1^\circ K.} = 28{,}882 \pm 50$ g.-cal.mole^{-1}.[15] This compares well with the value of $\Delta H^\circ_{298\cdot1^\circ K.} = 36{,}341 \pm 100$ g.-cal.mole^{-1} obtained[16-20] from spectroscopic measurements. The kinetics of the dissociation[21,22] and the recombination[23-25] have been studied at various temperatures and the reactions have been shown to be heterogeneous at low pressures but homogeneous at high pressures. From measurements of the effusion of iodine vapour, the equilibrium constant of this dissociation at 915°K. was calculated[26] as $\log K_p = 3\cdot7$. The potential energy of interaction of two iodine atoms as a function of the interatomic distance has been investigated and the force constants of the I–I bond discussed.[27-30]

The density of liquid iodine has been redetermined and is given by the expression $3\cdot94916 + 0\cdot003267(120 - t)$. The specific volume at 120°C. is 0·2532 ml.[31] Measurements of the density of solid iodine have been extended to low temperatures, $d_{78^\circ K} = 5\cdot15$ and the atomic volume at 0°K. obtained by extrapolation is 24·5 ml.[32]

The viscosity of iodine vapour at 60 mm. mercury pressure has been redetermined over the temperature range 380 to 800°C.:[33]

TABLE I. - VISCOSITY OF IODINE VAPOUR AT 60 mm. PRESSURE

T°K.	379·3	505·3	552·2	602·1	669·7	710·7	795·8
poise × 10^7	1785·0	2318·7	2561·0	2747·7	3064·5	3250·0	3604·0

These experimental results are in reasonable agreement with those calculated from the Sutherland equation.[33-35] The viscosity of liquid iodine at a temperature just above the melting point is 0·0198 poise compared with 0·0235 poise calculated by Andrade from Lindemann's equation.[36]

The coefficient of cubic expansion of solid iodine has been found to be $2\cdot64 \times 10^{-4}$ c.c.°C.$^{-1}$,[6] and that for liquid iodine $8\cdot54 \times 10^{-4}$ c.c.°C.$^{-1}$.[31]

The critical temperature of iodine has been determined as 553°C.[37] The most probable value for the melting point of iodine is 113·5°C.,[38] although it has been claimed that prolonged drying of the iodine may raise the melting point to 115·5°C.[39,40] The effect of capillarity on the melting point has also been studied.[41] The change in volume on fusion is 2·04%.[42] The vapour pressure of solid iodine has been redetermined using the gas current method:[43]

TABLE II.- VAPOUR PRESSURE OF SOLID IODINE DETERMINED BY THE GAS CURRENT METHOD

Temperature °C.	0	10	20	30	40	50
Vapour pressure mm. Hg.	0·02981	0·0798	0·1988	0·4643	1·0235	2·1419
Temperature °C.	60	70	80	90	100	–
Vapour pressure mm. Hg.	4·278	8·179	15·047	26·71	45·89	–

and also by a static method using a flexible metallic diaphragm:[44]

TABLE III.- VAPOUR PRESSURE OF SOLID IODINE DETERMINED BY A STATIC METHOD

Temperature °C.	29·967	40·017	50·154	60·119
Vapour pressure mm. Hg	0·46709	1·02614	2·21318	4·30723

These data are well represented by the equation:[43]

$$\log p_{\text{atm.}} = -\frac{3512{\cdot}8}{T} - 2{\cdot}013 \log T + 13{\cdot}3740.$$

The rate of evaporation of iodine into a vacuum has been measured.[45,45a] It is close to the calculated rate of bombardment of a surface in contact with iodine vapour at the corresponding saturated vapour pressure and it is concluded that all iodine molecules striking a solid iodine surface condense and that none are reflected.[45a] If a single crystal of iodine is suspended in a centrifuge, the rate of evaporation increases with centrifugal force, being directly proportional to the speed of the centrifuge.[46] The diffusion coefficient of iodine vapour has also been determined; between 14° and 30°C. it varies between 0·0767 and 0·0851 and gives a value for the radius of the iodine molecule of 2·923 A., which is lower than that computed from the viscosity measurements.[47] The rate and manner of condensation of iodine vapour on various surfaces has been shown to depend on the shape and nature of the condenser surface.[48-52]

The latent heat of fusion of iodine has been found to be 3740 ± 20 g.-cal. mole^{-1},[53] and the latent heat of vaporization, calculated from vapour pressure data, to be 14880·7 g.-cal.mole^{-1}.[44]

The heat capacity of iodine at constant pressure has been redetermined for the temperature ranges 10 – 50°K.[53] and 202 – 433°K.[54,55] For solid iodine, it can be expressed by the equation:

$$C_p = 13{\cdot}07 + 3{\cdot}21 \times 10^{-4}(t - 25)^2\ (\pm\ 0{\cdot}5\%)\ \text{g.-cal.mole}^{-1}$$

where t is the temperature in °C.[55] Above the melting point, the heat capacity has the values given in Table IV.[54]

TABLE IV.- HEAT CAPACITY OF IODINE ABOVE THE MELTING POINT

Temperature °C.	389.4	398.8	413.2	431.9	432.7
C_p g.-cal.mole^{-1}	20.00	19.72	19.00	18.70	18.02

The thermal conductivity of solid iodine has been found to remain practically constant at 0·001065 g.-cal.cm.$^{-2}$sec.$^{-1}$ between 24·4° and 42·86°C.[56] Using the heat capacity data, the standard entropy of solid iodine at 298·16°K. has been evaluated as 27·9 g.-cal.deg.$^{-1}$mole^{-1},[57-59] and that of gaseous iodine at 298·16°K. as 62·28 g.-cal.deg.$^{-1}$mole^{-1},[57-59] which compares favourably with the value of 61·81 calculated by statistical mechanics.[60] The chemical constant of molecular iodine has been evaluated on several occasions,[61-63] the most recent value being 3·91.[64] The standard entropy of gaseous, monatomic iodine is 43·18 g.-cal.deg.$^{-1}$mole^{-1},[57,65] and its chemical constant 2·00.[66] The thermodynamic data for iodine from 0 – 1700°K. have been recently reviewed.[67]

The molecular refractivity, R, of iodine vapour for a wave-length, λ, of 656·3 mμ. has been determined from 150 – 1030°C. for concentrations of $1-4 \times 10^{-5}$ g.c.c.$^{-1}$, the average value being approximately 31 c.c. Between 400° and 600°C., R begins to fall with rising temperature owing to the dissociation of iodine into atoms, and from this variation the atomic refractivity was calculated to be 13·4 ± 0·2 c.c. The atomic refractivity for λ equal to infinity is 12·5 ± 0·3 c.c.[68] The atomic refractivity of iodine has also been deduced from the refractive indices of many iodine-containing compounds[69,70] and for the C, D, F and G' lines is 13·825, 13·954, 14·310 and 14·620 c.c. respectively.[70]

Other forms of atomic volume, for example the atomic volume at zero fluidity[71-73] and the parachor,[74-77] have also been shown to be additive. The most recent value for the parachor of monovalent iodine in its compounds and in molecular iodine is 90·1 ± 0·2 c.c.,[78] and that for tervalent iodine is 73.[79] A quantity b defined by the empirical equation

$$b = M \log_{10} T + \frac{8{\cdot}0}{M}$$

where M is the molecular weight and T the boiling point of a substance in degrees absolute, has been shown to be additive. The contribution of iodine to b is constant and equal to 255.[80]

The thermionic emission from various metals in iodine vapour has been studied,[81-85] together with the effect thereon of temperature[86] and irradiation.[87,88] The relative abundance of the positive ions I^+, I_2^+ and I_3^+, formed by electron bombardment of iodine vapour, has been measured using a mass spectrograph.[89] Three negative ions, I^-, I_2^- and I_3^-, formed by the capture of slow electrons,[90-92] were also found in quantities comparable with those of the corresponding positive ions.[89,93] The commonest ionic species were I_2^- and I_2^+, by reason of the greater cross-section of the molecule for electron capture and also its greater concentration, as compared with the iodine atom.[93]

The critical potentials of iodine have been redetermined several times. The average value of the ionization potential of the iodine molecule is 9·8 ± 0·3 volts,[94-99] and that of the atom 8.0 volts.[98,99] Resonance potentials of the molecule are reported at 2·4 and 3·8 volts,[94,100] and of the atom at 1·0 and 6·5 volts[98-100] and, possibly, at 5·1 and 7·5 volts.[101] The ionization of iodine vapour by X-radiation,[102] by ultra-violet radiation[103] and by the addition of active nitrogen[104,105] has also been studied.

The electron affinity of an iodine atom is not so easily determined and is normally calculated, using the Born cycle, from the lattice and hydration energies of the alkali iodides.[106] Values of 69·9,[107] 72·4,[108] 73·6[109] and 76·3[109] kg.-cal.g.atom^{-1} have been recorded. Several calculations of the hydration energy of the iodide ion have been made[110-112] and, on the assumption of equal effective ionic radii of the potassium and fluoride ions, the hydration energy of the iodide ion has been evaluated as $\Delta G^{\circ}_{298\cdot1} = 70{\cdot}0$ kg.-cal.mole^{-1}.[113]

The ohmic resistivity of solid iodine has been measured using a tube of compressed crystals between graphite electrodes. The specific resistance, ρ, in ohms cm.$^{-1}$ at various temperatures[54] is shown in Table V. The specific resistance of liquid iodine at 121°C. is 19,900 ohms, the ratio of the resistivities of liquid and solid iodine at the melting point being 0·0237.[114] The

TABLE V. - SPECIFIC RESISTANCE OF SOLID IODINE

Temperature °C.	$\rho \times 10^{-8}$	Temperature °C.	$\rho \times 10^{-8}$
4·1	113·2	21·1	10·4
5·0	106·7	27·4	6·0
6·0	94·3	35·0	2·9
9·2	60·4	38·0	1·5
17·3	19·0	42·0	1·1

residual conductivity of liquid iodine is probably partly metallic or electronic and partly electrolytic, the current-carrying ions being I^+ and I^- or I_3^-, arising[115] from the self-dissociation

$$I_2 \rightleftharpoons I^+ + I^-$$
$$\text{or} \quad 2I_2 \rightleftharpoons I^+ + I_3^-.$$

The conductivity of iodine dissolved in liquid hydrogen sulphide,[116] in glacial acetic acid,[117] in benzene[118] and in nitrobenzene[117] is due to the same dissociation. The tri-iodide ion is an established species and its conductance, particularly in aqueous solution, has been carefully studied.[119-122] The existence of the I^+ ion has been proved in solutions of iodine monochloride, iodine trichloride[123] and iodine nitrate,[124] electrolysis of which gives iodine at the cathode. Liquid iodine dissolves many inorganic salts, particularly metal iodides, to give strongly conducting solutions.[125-128] The variation of equivalent conductance with concentration is quite abnormal, potassium iodide exhibiting a maximum value of 180 ohms^{-1} cm^2 at a molarity of 0·002 and sodium iodide a value of 2·6 ohms^{-1} cm^2 at a molarity of 0·0003, the value decreasing with increasing concentration.[128]

The dielectric constant of liquid iodine, determined by the resonance method, is 11·08 at 118·1°C. and 12·98 at 168°C.[129] Thus liquid iodine is one of the few liquids having a positive temperature coefficient of dielectric constant and does not obey the laws of Clausius–Mossotti and of Debye.[129-130] The dielectric constant of iodine vapour is stated to be always less than unity.[131,132] The dielectric constant of solutions of iodine in organic solvents has also been determined and used to calculate the dipole moment[133-136] of iodine. The average value for the polarization of iodine in c.c. in various non-polar solvents was found to be : *cyclo*hexane 31, benzene 38·5, *p*-xylene 47, *cyclo*hexene 56, 1,4-dioxan 66·5 and di-*iso*butylene 75, whereas that of iodine vapour is 32·2; the apparent dipole moments of iodine in these solvents were evaluated as 0·0, 0·6, 0·9, 1·1, 1·3 and 1·5 debyes respectively.[133] Since iodine has a symmetrical molecule, no permanent dipole would be expected, but some solvent molecules, themselves symmetrical and non-polar, can interact with iodine to give a polar complex. The bonding power of the solvents listed above is attributed to their π electrons and it is noteworthy that solutions of iodine in these solvents have a red or brown colour instead of the purple colour usually associated with solutions of iodine in indifferent solvents such as the aliphatic hydrocarbons and carbon tetrachloride.[133] The dielectric polarization of iodine in several solvents has been studied over the temperature range 15 – 60°C.[137] From the dielectric constants of solutions of numerous iodine-containing organic compounds, the contribution of a covalently bound iodine atom to the distortion polarization of a molecule was calculated as 13·2 c.c.[139]

Molecular iodine is diamagnetic, the specific susceptibility, χ, measured for a *cyclo*hexane solution being $-0{\cdot}35 \times 10^{-6}$ c.g.s. units.[140] Using other solvents, somewhat higher values are obtained[141] (see Table VI). This increase in apparent susceptibility is matched by a change in the colour of the solutions, the first three being violet, the last three being red or reddish-brown.

TABLE VI. - DIAMAGNETIC SUSCEPTIBILITY OF IODINE SOLUTIONS

Solvent	Diagmagnetic susceptibility $\chi \times 10^6$
Carbon tetrachloride	0·429
Chloroform	0·486
Carbon disulphide	0·538
Benzene	0·658
Toluene	0·667
Diethyl ether	0·677

It corroborates the suggestion, made in the paragraph dealing with dipole moments,[133] that in certain solvents iodine is not wholly non-polar and it is likely that interaction with the solvent is responsible for the discrepancy between the results tabulated above and the minimum value obtained in *cyclo*-hexane solution.[142,143] These values have been compared with the diamagnetic susceptibility calculated from Van Vleck's theory.[144] Using single crystals, solid iodine has been shown to be magnetically anisotropic, the specific susceptibility, χ, varying between $-0{\cdot}331 \times 10^{-6}$ and $-0{\cdot}389 \times 10^{-6}$ with varying orientation of the crystal.[145] The susceptibility of molecular iodine has also been measured at very low temperatures, 14·2° to 20·4°K., and has been shown to increase with falling temperature.[146] Atomic iodine is paramagnetic and on spectroscopic grounds a moment of 2 Bohr-magnetons has been suggested.[147] In order to measure the paramagnetic susceptibility of atomic iodine, a reasonable concentration of atoms is essential and temperatures higher than 1000°C. are normally required. The values of χ_M obtained at 1030 and 1127°C. were $8{\cdot}7 \times 10^{-4}$ and $11{\cdot}2 \times 10^{-4}$ c.g.s. units per mole respectively.[148]

The susceptibility of atomic iodine may also be calculated on the assumption that the contributions of the constituent atoms to the susceptibility of a molecule are strictly additive. On this basis, several calculations of the contribution of atomic iodine have been made,[149] the latest[150] value for χ_A being $-0{\cdot}512 \times 10^{-6}$. The most probable value for the diamagnetic susceptibility of the iodide ion is -57×10^{-6} c.g.s. units per g. ion in the vapour state and in the aqueous solution.[151-153] The magnetic rotatory power of atomic iodine is given as 143×10^{-2} and of the iodide ion as 450×10^{-2} minutes per unit field strength per g. atom.[154]

The standard oxidation-reduction potential of iodine in aqueous solution has been determined by measuring the potential of a platinum electrode with respect to a solution containing iodine, iodide and tri-iodide ions at known concentrations.[155-160] On the hydrogen scale, $E^\circ_{I_2/I^-}$ was found to be $+ 0{\cdot}5362$ international volt at 25°C. and $+ 0{\cdot}5340$ at 0°C.[158,160] The theory and use of the iodine-iodide electrode system in potentiometric titrations has been discussed.[161-164] The electromotive force of two iodine-iodide electrodes in the same alkali iodide solution is zero but if a centrifugal force is applied along the axis of the cell, a small electromotive force is generated from which the transport number of each ion may be calculated. The results agree to within 0·5 per cent. with those obtained by established methods.[165,166] The standard potential of the iodine-iodide electrode in methyl alcohol is reported as $+ 0{\cdot}357$ volt and in ethyl alcohol as $+ 0{\cdot}305$ volt, the standard of reference in each case being the hydrogen electrode.[167,168]

The cell,

$$\begin{array}{c|c|c|c|c|l} \text{Pb} & PbI_2 & Pb(ClO_4)_2 & Pb(ClO_4)_2 & PbI_2 & I_2(\text{Pt}) \\ \text{(5\% amalgam)} & \text{(solid)} & \text{(aq.)} & \text{(aq.)} & \text{(solid)} & \end{array}$$

has been proposed as a voltaic cell. It has a steady, reproducible electromotive force of 0·89360 international volt which remains constant for several months.[169] Storage batteries utilizing iodine have also been designed; they normally have a carbon anode, a zinc cathode and zinc iodide as electrolyte.[170,171]

The standard potential of the iodine-iodate electrode, i.e., the electromotive force of the cell

$$\begin{array}{c|c|l} H_2 & HIO_3(aq.) & I_2 \\ (1\ atm.) & (unit\ activity) & \end{array}$$

has been shown to be 1·195 international volts at 25°C. From this, the standard free energy of formation, $\Delta G^\circ_{298.1^\circ K.}$, of the iodate ion was evaluated as -32,251 g.-cal. g. ion^{-1}, and the standard heat of formation, $\Delta H^\circ_{298.1^\circ K.}$, as 54,996 g.-cal. g. ion^{-1}.[172]

Measurements have been made of iodine overpotential on smooth and platinized platinum and also on graphite. No systematic relation between current density and overvoltage was observed.[173] The contact potential difference at room temperature between a clean tungsten surface and an iodine-coated tungsten surface was found to be -0·91 volt.[174]

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SOLUTIONS OF IODINE IN NON-AQUEOUS SOLVENTS.[1,2]

Most of the solubility measurements previously recorded (Mellor, II, 85–88) have been repeated or extended and the more recent data are tabulated below:

TABLE VII. - SOLUBILITY OF IODINE IN NON-AQUEOUS SOLVENTS

Solvent	Temperature °C.	Solubility	Ref.
Benzene	25, 35, 50	14·09, 17·90, 25·51% W/W	3
Toluene	25	3·56% W/V	4
p-Xylene	25, 35	16·56, 20·13% W/W	5
*cyclo*Hexane	25, 35	2·72, 3·90% W/W	5
Pentane	−71	0·017% W/V	6
Heptane	0, 25, 50	0·618, 1·702, 4·196% W/W	3, 7
2:2-Dimethylbutane	0, 25, 35	0·48, 1·37, 1·99% W/W	5
*iso*Octane	24·92	1·303% W/W	8
Mesitylene	0, 25	13·51, 20·24% W/W	5
Ethyl alcohol	0, 25, 35	16·71, 21·43, 24·70% W/W	5, 9, 10
Propyl alcohol	18	6·8% W/V	10
Butyl alcohol	18	5·7% W/V	10
Diethyl ether	0, 25, 35,	19·34, 25·18, 18·50% W/W	5
Dipropyl ether	18	12% W/V	10
Dibutyl ether	18	7·7% W/V	10
Ethyl acetate	30	16·15% W/W	11
Propyl acetate	18	8·7% W/V	10
Butyl acetate	18	6·33% W/V	10
Propyl chloride	18	6·35% W/V	10
Butyl chloride	18	7·4% W/V	10
Propyl bromide	18	17·5% W/V	10
Butyl bromide	18	10·5% W/V	10
Methylene chloride	15, 25	4·22, 5·86% W/V	12
Chloroform	−60, 15, 25	0·089, 3·26, 4·52% W/V	12, 13
Carbon tetrachloride	−24, 0, 25, 50	0·257, 0·73, 2·91, 4·351% W/W	3, 12–17
Trichloroethylene	15, 25	2·80, 3·96% W/V	12
Tetrachloroethylene	15, 25	2·10, 3·06% W/V	12
cis Dichloroethylene	25	3·69% W/V	12, 18
trans Dichloroethylene	25	3·63% W/V	12, 18
Ethylidene chloride	25	3·82% W/V	12, 18
Monochloroethylene	15, 25	4·15, 5·47% W/V	12, 18
Pentachloroethane	15, 25	2·31, 3·09% W/V	12
Acetylene tetrachloride	15, 25	3·01, 4·10% W/V	12
Ethylene dibromide	10, 25, 70	6·85, 10·32, 33·20% W/W	8
Perfluoroheptane	0, 25	0·0025, 0·012% W/W	5
Carbon disulphide	0, 25, 35	7·70, 16·48, 21·62% W/W	5
Titanium tetrachloride	0·10, 25, 49·90	1·153, 2·855, 6·50% W/W	8
Silicon tetrachloride	0·01, 25, 40	0·256, 0·7433, 1·309% W/W	8
Carbon dioxide (under pressure)	25	0·208% W/W	19
Sulphur dioxide (under pressure)	50	0·6% W/W	20

In several cases, the solubility has also been measured at temperatures between those quoted above but such figures have been omitted for brevity. There is unfortunately a general lack of agreement between the results of different workers. Hildebrand has determined the mutual solubility of liquid iodine and carbon tetrachloride and shown that two liquid phases are formed with a critical solution temperature of 160°C.[21]

Refs. p. 839

The solubility of iodine in various mixtures of acetic acid and benzene has also been determined.[22] It dissolves readily in alcoholic solutions of potassium iodide to form potassium tri-iodide[23,24] (cf. page 837) and the densities, viscosities and surface tensions of these solutions have been recorded.[24] The concentration of iodine vapour, i.e., its partial vapour pressure, in saturated mixtures with nitrogen, oxygen, methane, carbon dioxide and the vapours of some common solvents has been measured[25] and its marked increase with applied pressure has been studied.[26]

Molecular weight determinations show that iodine is present in the diatomic state in all solvents. Nevertheless the anomalous dipole moment measurements (cf. page 829) and other physico-chemical studies indicate that in some solvents iodine is chemically bound to the solvent molecules and in equilibrium with atomic iodine. In all such solvents iodine forms brown solutions, quite unlike the normal violet solutions in which there is no evidence of interaction.[27] The approximate rate of exchange between iodine atoms and molecules in solution has been measured; the energy of activation for the exchange is probably between 2 and 3 kg.-cal.mole^{-1}.[28] Hildebrand has shown that iodine solutions in carbon disulphide, carbon tetrachloride, silicon tetrachloride and titanium tetrachloride are 'regular' solutions and his calculated values for the solubility of iodine in these solvents are very close to the observed values.[29] The equilibrium between dilute solutions of iodine and iodine vapour has been studied and the rates of evaporation and condensation measured. The condensation coefficient, α, was found to be between 10^{-3} and 10^{-5} at room temperature.[30] The rate of diffusion of iodine in organic solvents and solvent mixtures was measured to ascertain the degree of solvation of iodine but no conclusion could be drawn from the measurements except that the Stokes-Einstein equation was not applicable.[31] The densities of solutions of iodine in acetone, benzene, toluene, carbon disulphide and carbon tetrachloride are an approximately linear function of iodine content.[32] The variation of surface tension of several iodine solutions with iodine concentration and with temperature has been investigated[33-35] and a 0·5 M-solution in benzene shows distinct inflexions at 46 and 38°C., the latter probably corresponding to a previously undetected polymorphous transition point of iodine.[36]

SOLUTIONS OF IODINE IN WATER

Measurements of the solubility of iodine in water have been extended to 200°C. Above 112·3°C., in the presence of excess of iodine, two liquid layers are formed, the mutual solubility increasing with temperature:[37]

TABLE VIII.- MUTUAL SOLUBILITY OF IODINE AND WATER

Temperature °C.	126·5	155·4	187·4
Solubility of iodine in aqueous layer, %W/W	0·976	1·825	3·995
Solubility of water in iodine layer, %W/W	–	0·29	0·48

Iodine hydrolyses in water to give hypoiodous acid;[38]

$$I_2 + H_2O \rightleftharpoons HIO + H^+ + I^-.$$

From the pH of the solution, the hydrolysis constant,

$$K_h = \frac{[HIO] \times [H^+] \times [I^-]}{[I_2]},$$

has been computed as $4{\cdot}6 \times 10^{-13}$ at 25°C.[39] This value is obtained after allowing for the formation of the tri-iodide ion, $I_2 + I^- \rightleftharpoons I_3^-$, and is in reasonable agreement with the earlier conductometric value (Mellor, II, 78). Similar results have been obtained using the iodine electrode[40] and also by determining the error this hydrolysis introduces into the titration of aqueous iodine solutions with sodium thiosulphate.[41]

Iodine dissolves very readily in solutions of halogen acids to form complex polyhalide ions.[42,43] The solubility of iodine in hydriodic acid solution depends on the concentration of this acid and at 25°C. is given as follows:[44]

TABLE IX.- SOLUBILITY OF IODINE IN HYDRIODIC ACID SOLUTIONS

% Hydriodic acid	66·7	64·0	54·4	50·2	45·9
Solubility of iodine, kg. per litre	5·22	4·72	3·47	2·84	2·28

Conductance measurements show that the hydrogen tri-iodide formed is a typical, completely dissociated, strong electrolyte.[45] The equilibrium constant,

$$K = \frac{[I^-] \times [I_2]}{[I_3^-]},$$

determined in acid or neutral solution is $1{\cdot}35 \times 10^{-3}$ mole litre^{-1}.[46]

Iodine also dissolves in hydrobromic acid solutions forming $HBrI_2$. The solubility is proportional to the hydrobromic acid concentration and has been investigated over the temperature range 15 – 45°C.[47]

TABLE X.- SOLUBILITY OF IODINE IN HYDROBROMIC ACID SOLUTIONS

Molality HBr	3·1820	1·8507	1·2090	0·5880	0·1001
Molality I_2 at 25°C.	0·05192	0·03284	0·02109	0·01048	0·00319

The equilibrium constant,

$$K = \frac{[Br^-] \times [I_2]}{[BrI_2^-]},$$

is 0·073 mole litre^{-1}.[46] Similarly, iodine dissolves in hydrochloric acid solution, the solubility again increasing with acid concentration.[48] The equilibrium constant,

$$K = \frac{[Cl^-] \times [I_2]}{[ClI_2^-]}$$

is 0·28 mole litre^{-1}.[46]

Analogously, iodine is readily soluble in solutions of alkali halides, particularly iodides, to form polyhalides giving the ions $(XI_2)^-$, where X is chlorine, bromine or iodine.[49–51] The solubility of iodine in aqueous solutions of sodium, potassium, magnesium, strontium, cadmium and barium chlorides and bromides has been recorded.[52–55] In solutions of salts other than halides, however, iodine is less soluble that it is in water. This salting-out of iodine has been studied for solutions containing sulphate and nitrate,[56–58] and at low ionic strengths is less than that predicted by the Debye-McAulay formula.[58] It is suggested that salting-out of iodine also occurs in solutions containing halide and that the observed solubility is the net result of the combination of this effect with polyhalide formation.[56]

Various other physical properties of polyhalide solutions have been studied. The specific gravities of solutions of varying concentrations of iodine in 50% potassium iodide and of iodine solutions containing large excesses of potassium iodide and thallous iodide have been investigated.[59,60] Using the cell

Ag|AgI|0·01N-KI,I_2|Pt, the equilibrium constant for the iodide-tri-iodide equilibrium was found to be 1·40 × 10^{-3} mole litre^{-1} [61,46] Measurements of the evaporation of iodine from potassium tri-iodide solutions have shown that the loss of iodine is very small for low iodine concentrations, being proportional directly to iodine concentration and inversely to iodide concentration.[62-64]

Complete isothermal and polythermal analyses have been recorded for the ternary systems H_2O-I_2-MI, where M is sodium,[65,66] potassium,[67,68] rubidium,[69,70] caesium,[71,72] barium[73,74] and ammonium.[75] Numerous hydrated polyhalides of the type MI_3,xH_2O, MI_5,xH_2O and MI_7,xH_2O were isolated as solid phases, but anhydrous solid tri-iodides were found only in the cases of rubidium, caesium and ammonium. Attempts to prepare anhydrous potassium polyiodides from benzene solution resulted in the formation of the solvates KI_3,C_6H_6 and $KI_5,2C_6H_6$.[76] Polyiodides are not formed when the iodides of lithium, potassium, rubidium and thallium are fused with iodine, and this observation demonstrates the important role of the solvent in polyiodide formation.[77,78] Instead of a tri-iodide, a solid solution of iodine in the metal iodide is obtained, the crystals of which show a high degree of electronic conductance.[79,80] Iodised sodium chloride is used to supplement the normal iodine content of animal and human foodstuffs and the factors affecting the rate of loss of iodine by evaporation from this material in preparation and in storage have been investigated.[81-83]

BINARY SYSTEMS INVOLVING IODINE

The solubility of iodine in cuprous iodide has been investigated and shown to decrease in the presence of other iodides.[84] Thermal analysis of the system AlI_3-I_2 shows a eutectic at 94°C. corresponding to a composition of 67 mole% of iodine.[85] Both the systems AsI_3-I_2 and SbI_3-I_2 show simple eutectics, and no sign of pentaiodide formation was observed in either case.[86] For SnI_4-I_2 mixtures, a simple eutectic was also observed at 77·8°C., its molar composition being SnI_4 + 3·257 I.[87] The systems PCl_3-I_2, PBr_3-I_2, P_2I_4-I_2, PCl_5-I_2 and PBr_5-I_2 have been studied in detail. Compound formation does not take place with phosphorus trichloride, tribromide or tetraiodide, although the last named compound does undergo a slow conversion to the tri-iodide, $P_2I_4 + I_2 = 2PI_3$. The electrical conductivity of these systems in the molten state is in each case less than that of molten iodine. The addition of phosphorus pentabromide to iodine lowers the melting point to 13·5°C., corresponding to a eutectic of 50 mole% of PBr_5. On the addition of further pentabromide, the melting point rises to a maximum of 110°C. at 75 mole% of PBr_5 and then falls to the melting point of phosphorus pentabromide, 103·7°C. The maximum is attributed to the reaction $3PBr_5 + I_2 \rightleftharpoons PBr_3 + 2PBr_6I$. The system PCl_5-I_2 is very similar and the maximum melting point is identical with that of an equimolecular mixture of phosphorus pentachloride and iodine monochloride, where it is also assumed that PCl_6I is formed. The specific gravities of these phosphorus halide-iodine systems have also been measured.[88] The binary systems of iodine with sulphur,[89-91] selenium[91] and tellurium[92] afford no evidence of compound formation. The existence of sulphur iodide, S_2I_2, has been reported, but it is likely that only a solid solution of iodine in sulphur was obtained.[93-95] With iodoform iodine forms an ideal solution,[95,96] but with naphthalene a eutectic is formed.[96,97]

The binary systems iodine-iodine monochloride[98] and iodine-bromine,[99] and the ternary system iodine-bromine-chlorine[100] have been studied. In the latter case, the solid phases obtained at 29·8°C. were iodine monobromide, iodine trichloride and solid solutions of iodine and iodine monobromide. No ternary compound was detected. The lattice spacing in the iodine-bromine solid solutions was found to change linearly with composition.[99]

Refs. p. 839

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THE ADSORPTION OF IODINE

Iodine is reversibly adsorbed on platinum[1,2] and gold[3] and up to 1000°C. a monomolecular layer is formed. Above this temperature there is an increasing tendency in the case of platinum for chemical reaction to occur[4] (see page 849). The chemisorption of iodine on metals such as copper and silver is discussed elsewhere (see page 848).

J. H. de Boer and his co-workers have made a detailed study of the adsorption of iodine vapour on metal halide crystals and on crystalline films, particularly those of calcium fluoride[5-13] and barium chloride.[14] The adsorption isotherms of iodine on both these salts are sigmoid, in agreement with the Brunauer–Emmett–Teller multilayer adsorption theory,[15] although surface areas calculated from the theory are between one half and one quarter of the true surface area as determined by chemisorption of water or reaction with alizarin vapour. Hence the layers are considered to be unimolecular.[16] As might be expected, iodine is adsorbed by metal iodides. With potassium iodide, the adsorbed layer is 2 molecules thick but there is no evidence of the formation of the tri-iodide.[17] It has been reported that thallous iodide adsorbs 2g.-atoms of iodine per mole TlI, but no direct evidence of the formation of thallous tri-iodide was found.[18] From the absorption spectrum of iodine adsorbed on thallous iodide, it was concluded that under the influence of light photodissociation, but not desorption, of the iodine molecules occurs.[19,20] Iodine has been shown to be reversibly adsorbed on cuprous iodide, the concentration of adsorbed iodine varying with the square root of the iodine vapour pressure.[21,22] The electrical conductivity of the cuprous iodide at 132·1°C. increased approximately as the 4/3rd power of the concentration of adsorbed iodine.[22] The adsorption of iodine on the oxides of magnesium,[23,24] aluminium,[25] zinc[24] and antimony,[24] on calcium hydroxide,[24] on strontium and barium carbonates[25] and on barium sulphate[25] has been determined. The effect of pre-treatment of these solids was investigated and it was concluded that with the oxides and the carbonates irreversible chemisorption takes place.[24]

Adsorption isotherms of iodine vapour on porous materials such as activated charcoal[26,27] and silica gel[28,29] have been determined. The adsorption has been shown to follow the same laws as the adsorption of vapours of liquids even at temperatures well below the normal melting point of iodine.[30] A proposed mathematical formulation of the rate of penetration of iodine vapour into a reactive porous medium is based on the assumption of a reaction front behind which the concentration of vapour retains its initial value but in front of which the concentration is zero. This gives good agreement with observed rates.[31] The adsorptive capacity of charcoal depends markedly on its mode of preparation, being particularly sensitive to the presence of small amounts of inorganic salts.[32-34] The adsorption of iodine on glass and quartz surfaces from 15° to 1000°C. has been determined using an interferometer. Between 150° and 400°C. and between 850° and 1000°C., the logarithm of the quantity of iodine adsorbed is a linear function of the reciprocal of the absolute temperature, indicating low temperature and high temperature types of adsorption with heats of adsorption 1·2 and 15 kg.-cal.mole^{-1} respectively.[35] Atomic iodine on coming into contact with quartz glass produces a brown coating which has been identified as silicon.[36] The adsorption of hydrogen and nitrogen[37] and various solvent vapours[38] on crystalline iodine has been investigated. In the latter case, normal adsorption occurs before disruption of the solid lattice by the solvent.

Iodine in solution is strongly adsorbed by charcoal and other porous materials: 100g. of activated charcoal can adsorb up to 60g. of iodine. Much work has been done on the relative adsorptive capacity of different types of charcoal for iodine dissolved in many solvents, particularly in benzene, chloroform and carbon tetrachloride.[39-59] It has been shown[60-63] that the adsorption is in accord with the Freundlich adsorption isotherm, even in mixed solvents[64] and in viscous media.[65] On the assumption that a monolayer is formed, the adsorption of iodine from solution affords a convenient method for determining the effective surface areas of solids.[66] The quantity of iodine adsorbed per unit weight of charcoal depends on the solvent in which the iodine is dissolved, being progressively greater in the order: water < polar organic solvents < non-polar organic solvents.[67] The extent of adsorption has been semi-quantitatively correlated with the dielectric constant[68] and other properties of the solvent[69] and solution.[70] Any variety of charcoal can be rendered more adsorptive, i.e. activated, by pretreatments such as heating in steam,[71] soaking in organic solvents[72] or exposure to chlorine.[73] Dilute solutions of oxidizing agents such as potassium permanganate also activate the charcoal but concentrated solutions do not.[74] Simply heating the charcoal has little effect on its activity.[75] The adsorptive power of activated charcoal and the effect of its preparation and pretreatment have been discussed in terms of the existence of several species of active centres and the variation in their numbers.[76] An equation for the lowering of the melting point of a substance adsorbed within a porous solid has been developed:

$$\frac{T_\infty - T}{T_\infty} = \left(\frac{2v}{rq}\right)\sigma\cos\phi,$$

where T_∞ is the normal melting point, T the melting point within the porous solid, v the molar volume of the liquid phase, r the radius of the pores, q the heat of fusion, σ the liquid–gas interfacial tension and ϕ the angle of contact between the liquid substance and the inert porous solid. It was used to show that iodine contained in active charcoal is still liquid at room temperature.[77]

Iodine in solution is also strongly adsorbed on silica gel.[78,79] The adsorption of iodine from carbon tetrachloride solution on microscopic glass spheres of known surface area has been measured and, assuming a monomolecular adsorbed layer, it appears that only 39% of the glass surface is covered.[80]

The adsorption of iodine from solution on magnesium oxide has been shown to depend on the age and pretreatment of the oxide and particularly on the solvent used.[81,82] The adsorption of iodine on activated alumina,[83,84] on barium sulphate,[85] on silver iodide[86] and on various clays[87] has been studied.

Though the reaction between aqueous solutions of iodine and starch to give the characteristic blue complex has been studied for the last 150 years or more, it is still under active investigation.[88-93] At low concentrations of iodine the interaction is one of reversible adsorption and the iodine can be extracted by solvents such as chloroform.[94] With higher concentrations of dissolved iodine the interaction is only slowly reversible and it is now considered that the iodine is contained inside the helical form of the linear amylose component of starch, the quantity of iodine taken up increasing with the length of the helices.[95,96] Branched chain and short chain amyloses, such as amylopectin, take up much less iodine to form unstable red or brown complexes.[97] The blue complex between iodine and starch of the long chain amylose variety has been studied potentiometrically,[98-101] spectrophotometrically[102,103] and by means of X-rays.[104,105] In order to obtain a sufficient concentration of iodine in solution, the presence of an alkali iodide is normally necessary and some of the iodine is taken up as the tri-iodide ion although, contrary to many assertions, the blue complex can be obtained with iodine alone.[106-109] Potentiometric titrations have shown that when iodine is added to amylose solutions its activity remains very low and nearly constant until one iodine molecule for every 6 to 8 glucose residues in the amylose has been added, the exact figure depending on the iodide concentration.[98-101]

It was suggested[95,96] that the iodine is 'dissolved' in the hydrocarbon groups which line the interior of the amylose helix, but the deep blue colour of the complex and its absorption spectrum indicate that the iodine is not just in non-polar solution. An alternative proposal is that the iodine molecules and the tri-iodide ions acquire an induced dipole inside the dipolar helix and are oriented parallel to one another and to the axis of the helix, the effect increasing with the length of the helix. The polarization of the iodine molecules alters its light-absorption characteristics and gives rise to the characteristic blue colour.[97-101] A more recent explanation of the blue coloration, based on experiments using the iodine isotope ^{131}I, is that it results from a change in the starch molecule induced by iodine acting catalytically in the presence of oxygen and is not dependent on the presence of iodine as such.[110]

The partition of iodine between aqueous solutions and organic solvents such as carbon tetrachloride,[111-116] chloroform,[111] carbon disulphide,[111,117,118] petroleum[119] and ether[120] has been further studied.

The partition coefficient of iodine between carbon tetrachloride and heavy water, D_2O, is 103 at 25°C., as compared with 85 for normal water.[116] Its distribution in completely miscible liquids diffusing together has also been determined.[121] Iodine has been used as an effective emulsifying agent for mixtures of ethyl ether, ethyl acetate, amyl acetate and amyl alcohol with water.[122]

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THE ATOMIC WEIGHT OF IODINE

The atomic weight of iodine has been determined by a variety of methods, and all yield very similar results. By synthesizing silver iodide from pure silver and iodine, the mass ratio of silver to iodine and of silver iodide to silver chloride was determined[1] and taking Ag = 107·880, the atomic weight of iodine was found by Hönigschmid and Striebel[2] to be I = 126·917 ± 0·0013. This work was later repeated by Baxter, Titus and Lundstedt[3,4] who obtained I = 126·915. A value I = 126·915 had been obtained much earlier (1914) by Guichard[5] from the analysis of very pure iodine pentoxide and although much lower results were subsequently obtained by Baxter and Butler[6] and Baxter and Hale[7] using this method, it was later pointed out by Moles[8] that the discrepancy arose from the application of buoyancy corrections based on faulty data for the density of iodine pentoxide. Several redeterminations of this density were then carried out and values between 4·98 and 5·28 were obtained.[8,9] Using this last figure, Moles recalculated the results of Baxter and Butler and obtained the value I ≐ 126·917. Thus it appears that all the chemical methods of determining the atomic weight of iodine afford values in substantial agreement.

Physical methods of determining the atomic weight also give similar results.[10] From vapour density measurements, Moles obtained the value I = 126·92.[11] Aston used the mass spectrograph to demonstrate the absence of isotopes of iodine, to measure its packing fraction and hence to determine its atomic weight.[12] More recent determinations of the packing fraction give results of $-4{\cdot}2 \times 10^{-4}$,[13] and $-4{\cdot}4 \times 10^{-4}$,[14] which correspond with atomic weights I = 126·912 and 126·909 respectively. The discrepancy between these figures and the results of chemical determinations might be due to analytical errors or to an incorrect value of the atomic weight of silver. It seems likely, however, that as the values of the packing fraction were estimated by a somewhat difficult interpolation the atomic weights obtained by chemical analysis or synthesis are probably the more accurate.[15] By means of *X*-rays, Straumanis measured the volume, V, and the number of atoms, n, comprising the unit cell of solid iodine. These are related to the atomic weight by the equation:

$$\text{At. Wt.} = \frac{NdV}{n}$$

where N is the Avogadro number and d the density; the low value of 126·80 was obtained. However none of the values for the density of iodine at room temperature are at all recent and it is possible that a fresh value of d would yield a higher value for the atomic weight.[16]

Much of this work has been critically reviewed by the several committees on atomic weights set up by the International Union of Pure and Applied Chemistry: the most recent accepted value for the atomic weight of iodine is I = 126·92.[17]

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CHEMICAL REACTIONS OF IODINE

The extensive work on the reversible reaction of iodine with hydrogen, $H_2 + I_2 \rightleftharpoons 2HI$, has been reviewed by Bodenstein[1] and by Hinshelwood.[2] Complete thermodynamic data for this reaction from 0 – 1500°K. have been tabulated by the United States National Bureau of Standards[3] and a few values (in kg.-cal.mole^{-1}) of the standard heat content change, ΔH°, the standard free energy change, ΔG° and of the equilibrium constant (expressed as $\log_{10}K$) are given in Table XI.

TABLE XI. - THERMODYNAMIC DATA FOR THE REACTION

$\frac{1}{2}H_2 + \frac{1}{2}I_2 \rightleftharpoons HI$

Temperature °K.	ΔH°	ΔG°	$\log_{10}K$
298·16	–1·24	–2·01	1·472
300	–1·24	–2·01	1·465
500	–1·43	–2·47	1·081
1000	–1·69	–3·39	0·742
1500	–1·72	–4·74	0·617

The reaction is bimolecular and at 700°C. has a velocity constant of $6{\cdot}4\times10^{-2}$ mole litre^{-1}.[2] Measurements of the variation of the velocity constant with temperature lead to an activation energy for the reaction of 43·3 kg.-cal. mole^{-1}.[1,2] It is suggested that this is largely the energy required to dissociate the iodine into atoms which then rapidly react with molecular hydrogen.[4-7] There is no evidence that the reaction is influenced by the presence of water vapour.[8,9] Both forward and reverse reactions are photosensitive although the formation of hydrogen iodide is not catalyzed by wave-lengths longer than 3100 A.[10] Hydrogen is readily adsorbed by solid iodine in an electric discharge tube.[10a]

The reaction of iodine with deuterium is slower than with hydrogen,[11] the ratio of the rate constants K_{H_2}/K_{D_2} at 760°C. being 2·15.[12] The activation energy of the deuterium reaction was found to be 46·6 kg.-cal.mole^{-1} but if the difference in the collision rate is considered, the difference in the activation energies was calculated to be only 750 g.-cal.mole^{-1}.[12] This work was later criticized.[13] Both these reactions are considered further in the section dealing with hydrogen and deuterium iodides.

Iodine vapour combines at room temperature with the vapours of the alkali metals in a highly luminous reaction.[14-18] The emission spectra of these dilute flames have been recorded[15-18] and a significant emanation of electrons has been detected.[19] The interaction of a beam of iodine molecules[20] with a beam of cadmium atoms at very low pressures has also been investigated.[21]

Iodine as vapour or in the solid state reacts at room temperature with copper and silver to form cuprous iodide and silver iodide respectively. The rate and manner of formation of the iodide layers on the metals were studied by observing the interference phenomena resulting from the reflexion of light in the thin layers[22-28] and by measuring the variation of surface potential.[29] The rate of tarnishing of the metal surfaces in iodine vapour was found to be considerably increased when a beam of ultrasonic sound was directed onto the surfaces.[30] The reaction between copper and iodine in aqueous potassium iodide solution is unimolecular with respect to the iodine concentration and the rate is not affected by varying thicknesses of the cuprous iodide film on the surface,[31] whereas the rate of the corresponding reaction in an organic solvent certainly is so affected.[32] The reaction of tin with iodine in carbon tetrachloride solution is unimolecular but depends on the rate of diffusion of iodine to the metal.[33] The rate of reaction of iodine with mercury vapour[34] and with mercury droplets[25,35] has been studied. In the second case, the reaction is heterogeneous and is very rapid when a crystal of mercuric iodide is in contact with the mercury surface. The first product of the reaction is mercurous iodide and, in the presence of further iodine, this is transformed into mercuric iodide: $2Hg + I_2 \rightarrow Hg_2I_2$; $Hg_2I_2 + I_2 \rightarrow 2HgI_2$.[35]

Iodine as vapour and in the solid state reacts with magnesium, calcium, aluminium, zinc, tin, nickel and iron and in each case the iodide is formed.[36,37] No reaction has been observed with lead, bismuth or gold.[37] Platinum is also unattacked by iodine at ordinary temperatures but at 1400°C., when appreciable dissociation of the iodine into atoms occurs, volatile PtI and PtI_2 are formed. The heat of adsorption of atomic iodine on platinum is calculated to be 53·7kg.-cal.mole^{-1}.[38] Tungsten, on the other hand, is attacked by molecular iodine at normal temperatures to form a non-volatile iodide but is not attacked at high temperatures when even atomic iodine has no effect.[38] Iodine reacts with both tantalum and niobium at 1300 – 1500°C. to form the pentaiodides, TaI_5 and NbI_5 respectively. If the surrounding iodine vapour is heated above 400°C., the iodides distil off and in each case a black distillate of uncertain composition is collected.[39] Iodine and vanadium combine to form the pentaiodide, VI_5, which on heating decomposes to garnet red crystals of the sesqui-iodide, V_2I_3. This does not decompose or vaporize on further heating.[39]

Moist iodine vapour rapidly corrodes metals, including most stainless steels.[40-45] The initial process is the formation of corrosion centres where small amounts of metal iodide are formed which invariably deliquesce, and the major part of the corrosion then takes place in the liquid phase, almost certainly electrochemically.[41] The effect of water vapour pressure,[40] iodine vapour pressure and temperature[43] on the rate and manner of formation of corrosion centres has been studied for the metals beryllium, aluminium, copper, iron and some steels. Only titanium and molybdenum steels were unattacked.[44,45] The corrosion of metals by molten iodine has also been investigated.[46] Moist iodine reacts slowly with iron carbide forming ferric polyiodide and ferric iodate.[47] In the presence of aqueous ethyl alcohol, aluminium and iodine form aluminium iodide, AlI_3, which hydrolyses:

$$AlI_3 + 3H_2O \rightarrow Al(OH)_3 + 3HI.$$

The hydriodic acid in the presence of more aluminium then reacts with the ethyl alcohol to give ethyl iodide.[48]

Iodine and oxygen combine to form iodine pentoxide but only under high pressures and at high temperatures. After 2 hours at 325°C. and 1200kg.per sq.cm. partial pressure of oxygen, a yield of 2·3% was obtained.[49] The reaction between iodine and carbon monoxide, $CO + I_2 + H_2O = CO_2 + 2HI$, has been shown to occur in acid solution and to be strongly catalysed by palladous salts.[50] Phosphorus vapour and dry iodine vapour react to form phosphorus tri-iodide, PI_3.[51] The same product is obtained when the reaction is carried out in carbon disulphide solution provided that water and oxygen are rigorously excluded,[52] but in carbon tetrachloride solution only the tetraiodide, P_2I_4, is formed.[53] The addition of water to the reaction product in carbon disulphide gives phosphonium iodide.[54]

Iodine dissolves unchanged in absolute sulphuric acid[55] and its solubility is increased by the addition of anhydrous silver or mercuric sulphates.[56] Such solutions are strongly oxidizing, probably because compounds of the type $I_2(Ag_2SO_4)_3$, $I_2(AgHSO_4)_6$ or I_2SO_4 are present.[56] The suggestion that the oxidizing power of these solutions is due to the formation of hydrogen peroxide is thought to be incorrect.[57] Sulphurous acid is quantitatively oxidized by iodine to sulphuric acid;[58-60] the reaction is very fast and special techniques are required to study its kinetics.[59,60]

The reaction of iodine with concentrated nitric acid to form iodine pentoxide is well known[61,62] and it has been shown that at least 88·5% HNO_3 is required for the reaction to proceed to completion within one hour.[62] With fuming nitric acid, the first product of the reaction is iodine tetroxide, I_2O_4, which is decomposed by further heating or by reaction with water to yield iodine pentoxide, I_2O_5. If moisture is rigorously excluded from the reaction and the oxides of nitrogen are removed as they are formed by a current of air, the decomposition is prevented and iodine tetroxide can be isolated.[63-65]

Nitrous acid and nitrites are quantitatively oxidized by iodine to nitric acid and nitrates respectively: $NaNO_2 + I_2 + H_2O = NaNO_3 + 2HI$. The reaction is bimolecular in the dark, the reaction rate being given by

$$-\frac{d[\Sigma I_2]}{dt} = k\frac{[NO_2^-][\Sigma I_2]}{(K_3+[I^-])\left(A\frac{[I^-]^2}{[NO_2^-]}+1\right)}$$

where k and A are constants and K_3 is the equilibrium constant for tri-iodide formation. The kinetics of the reaction indicate that the mechanism involves iodine atoms, nitrogen peroxide and regenerated nitrous acid:[66]

$$NO_2^- + I_2 \rightleftharpoons NO_2 + I^- + I$$

$$NO_2^- + I \rightleftharpoons NO_2 + I^-$$

$$2NO_2 + H_2O \rightleftharpoons HNO_2 + HNO_3.$$

The reaction between iodine and neutral nitrites, normally slow, is accelerated by the presence of sodium thiosulphate, and in iodometric titrations nitrites and oxides of nitrogen must be rigorously excluded.[67] The oxidation of nitrites by iodine is photosensitive and several investigations of the quantum efficiency and temperature coefficient of this reaction have been carried out.[68-73] The quantum yield was found to be independent of the initial iodine concentration but dependent on the wave-length of the incident radiation, on the temperature and on the total ionic strength. It is always considerably less than unity, being normally within the range 0·005 – 0·1.[68] Iodine reacts with molten potassium nitrite to give potassium nitrate and nitric oxide, $I_2 + 4KNO_2 = 2KNO_3 + 2KI + 2NO$.[74]

The reaction of iodine with hyponitrites depends on the pH of the solution. In alkaline solution, nitric oxide and a nitrite are formed, whereas in neutral or acid solution nitrogen and nitrous oxide are formed as well.[75] In alcoholic solution, iodine reacts with silver nitrate to give silver chloride and iodine nitrate: $AgNO_3 + I_2 = AgCl + INO_3$. The iodine nitrate may be isolated as the pyridine or quinoline salt.[76]

Iodine reacts with phosphoric acid in fuming nitric acid solution, iodine phosphate, I_3PO_4, being formed.[77,78] Phosphorous acid is oxidized slowly by iodine: $H_3PO_3 + I_2 + H_2O = H_3PO_4 + 2HI$.[79-81] Between pH 2 and pH 9 the only detectable reaction was between HPO_3^{--} ions and free iodine molecules. When treated on the basis of a simple collision hypothesis, this bimolecular reaction falls into the category of reactions having abnormally high values of P in the equation

$$k = PZe^{-E/RT};$$

the value in this case being 3×10^7. At pH values less than 1 the reaction becomes much faster and the acid-catalysis is thought to be due to the formation of protons solvated by undissociated phosphorous acid molecules, i.e. $H_4PO_3^+$, which are highly active.[81] The reaction of iodine with hypophosphorous acid and hypophosphites, although much faster, probably has a similar mechanism.[82-85] It is also acid-catalyzed, almost certainly through the formation of $H_4PO_2^+$. For the reaction $H_3PO_2 + I_2 + H_2O = H_3PO_3 + 2HI$, the velocity constant at 30°C. is 0·35 and the activation energy is 20 kg.-cal.mole^{-1}, whereas for the phosphite reaction the corresponding quantities are 0·001 and 22·5 kg.-cal.mole^{-1} respectively.[85]

Iodine reacts with concentrated ammonia solution to give nitrogen tri-iodide $N_2H_3I_3$.[86] With warm dilute aqueous ammonia, iodine forms ammonium iodide and a small amount of ammonium iodate, and nitrogen is evolved.[87] It is probable that ammonium iodide formed initially reacts with more iodine to form monoiodoamine, $NH_2.I$, i.e., $NH_4I + I_2 = NH_2I + 2HI$. The monoiodoamine, being unstable, then decomposes according to the equation $4NH_2I = 2NH_4I + N_2 + I_2$.[88] The reaction between iodine and ammonia in carbon tetrachloride solution results mainly in an addition product xNH_3,yI_2, although small quantities of hydrazine and hydroxylamine have also been detected.[86]

The rate of reaction of iodine with alkali metal hydroxide solutions to give the corresponding hypoiodite has been shown to increase with the concentration of alkali and with rising temperature. At 50°C. the reaction is almost instantaneous: $2NaOH + I_2 = NaI + NaOI + H_2O$. The subsequent transformation of the hypoiodite into iodate is, however, little influenced by these factors or by the concentration of iodate.[89,90] Magnesium oxide and calcium oxide develop a red colour in iodine solutions. The iodine is thought to be chemisorbed although some formation of hypoiodite occurs. In organic solvents iodine is also adsorbed on these oxides and reacts slowly to form the metal iodide and iodate.[91] With silver and mercuric oxides, addition products are formed, Ag_2OI_2, a green amorphous powder[92] and $HgOI_2$, a red amorphous powder.[93] Both compounds decompose in boiling water or in alkaline solution to give a mixture of of iodide and iodate: $3AgOI_2 + 6KOH = 6AgOH + KIO_3 + 5KI$. Nascent iodine in the presence of hydriodic acid reacts with alkali and alkaline earth oxides, silver oxide, mercuric oxide, and nickel and copper hydroxides to form the corresponding iodides.[94] Thermally or optically dissociated iodine vapour reacts with quartz glass and produces a brown coating identified as silicon but in the presence of oxygen the coating is essentially silica.[94a]

Iodine reacts with hydrogen peroxide solution to give hydriodic acid and oxygen, $I_2 + H_2O_2 = 2HI + O_2$, but the acid, once formed, is rapidly oxidized by the hydrogen peroxide liberating free iodine, $HI + H_2O_2 = 2H_2O + I_2$. The iodine therefore catalyzes the decomposition of the peroxide and, by adjusting the concentrations in this reaction, a steady state may be attained where the rate of formation of iodine equals the rate of its removal. The reaction between iodine and hydrogen peroxide is infinitely slow in acid solution but attains a measureable velocity in neutral solution and becomes very fast in alkaline solution. There is at least a two-fold mechanism (1) $I_2 + H_2O \rightarrow HI + HIO$ and (2)$HIO + H_2O_2 \rightarrow HI + H_2O + O_2$.[95-98] The rate-determining step is the hydrolysis of iodine, (1), and the second step, the reaction of IO^- with a molecule of hydrogen peroxide is very fast, the specific reaction rate being 4×10^{11}.[98] The reaction mechanism is, however, almost certainly more complex;[99-102] when iodine in solution is treated with a moderate excess of hydrogen peroxide, there is a lengthy induction period which may be curtailed by adding acid, or eliminated by addition of a small quantity of an iodate.[103] The reaction is photo-sensitive and the effect of changing concentrations of the reactants on the quantum yield has been determined. The primary step in the light-catalyzed chain reaction is the dissociation of the iodine into atoms; these then react with the hydrogen peroxide to form the HO_2 radical which with the molecular iodine forms oxygen, hydriodic acid and another iodine atom. (1) $I_2 + h\nu \rightarrow 2I$; (2) $H_2O_2 + I \rightarrow HO_2 + HI$; (3) $HO_2 + I_2 \rightarrow HI + I + O_2$.[104]

Iodine oxidizes arsenious oxide in aqueous solution to arsenic acid: $2I_2 + 5H_2O + As_2O_3 = 4HI + 2H_3AsO_4$. The essential step in the reaction is between HIO, formed by hydrolysis of the iodine, and the undissociated molecules of arsenious acid, H_3AsO_3.[105,106] The reaction is reversible although the equilibrium concentration of arsenious acid is normally very small.[106] In neutral solution this reaction is the basis of an accurate method of standardizing iodine solutions. Iodine also oxidizes arsenious sulphide, and in alkaline solution arsenate and sulphate are produced:

$$As_2S_3 + 14I_2 + 40NaOH = 2Na_3AsO_4 + 3Na_2SO_4 + 28NaI + 20H_2O.$$

Molybdenum trisulphide is similarly oxidized to molybdate and sulphate. Both reactions are quantitative in strongly alkaline solution and may be used for the determination of these sulphides.[107] The reaction between iodine and hydrogen sulphide in aqueous solution is a useful method of preparing pure hydrogen iodide; $H_2S + I_2 \rightarrow 2HI + S$.[108] The fact that it does not take place in carbon tetrachloride and certain other non-aqueous solvents has been confirmed, although pyridine has been shown to be as effective as water in promoting rapid and complete reaction.[109]

The oxidation by iodine of thiosulphates to tetrathionates is the basis of most iodometric titrations and the exact conditions needed to attain true equivalence have been studied.[110,111] In aqueous solution the reaction is very fast but measurable rates were obtained by mixing aqueous sodium thiosulphate solutions with solutions of iodine in carbon tetrachloride and in chloroform.[112-4] The presence of nitrite ions has been shown to catalyze the conversion of thiosulphate to sulphate and not to tetrathionate.[115,116] Iodine also reacts with solid sodium thiosulphate but only when this salt has one or more molecules of water of crystallization.[117]

In neutral solution iodine quantitatively oxidizes thiocyanates to the corresponding sulphate and iodine cyanide:

$$2KCNS + 8I_2 + 8H_2O \rightarrow K_2SO_4 + 2ICN + 14HI + H_2SO_4.$$

In acid solution, owing to the displacement of the equilibrium $ICN + I^- \rightleftharpoons CN^- + I_2$, the net reaction is:

$$2KCNS + 6I_2 + 8H_2O \rightarrow K_2SO_4 + 12HI + 2HCN + H_2SO_4.$$

A kinetic examination[118] of this oxidation has shown that the mechanism is not as simple as was first thought,[119,120] although there is little doubt that the reaction is strongly base-catalyzed.[118-120] Excess of alkali, however, causes hydrolysis of the iodine cyanide and in quantitative analysis the reaction is best carried out in the presence of sodium bicarbonate.[120]

The oxidation by iodine of ferrous iron to the ferric state occurs only under the influence of light. In the dark, the reverse reaction occurs.[121-123]

$$2Fe^{2+} + I_2 \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} 2Fe^{3+} + 2I^-.$$

The only photosensitive reactant involved is iodine, which undergoes photodissociation.[124-129] In the visible region, wave-lengths of 5500 to 6500 A. are effective[124] and ultra-violet radiation also has been shown to promote the forward reaction.[125] The velocity constants of the forward and back reactions and the equilibrium constant have been studied, also the effect of added salts.[130-134] The forward reaction can be brought to completion by adding phosphoric acid whereby the feebly ionized ferric phosphate is formed.[135] Iodine also oxidizes tervalent titanium to the tetravalent state,[136] divalent manganese to trivalent manganese[137] and tervalent vanadium to tetravalent vanadium.[138] A step-wise mechanism for these reactions has been proposed, *e.g.*, (1) $Ti^{3+} + I_2 \rightleftharpoons Ti^{4+} + I_2^-$ (2) $Ti^{3+} + I_2^- \rightarrow Ti^{4+} + 2I^-$.[139]

Metallic cyanides react with iodine to form the corresponding iodides and cyanogen: $I_2 + 2CN^- = C_2N_2 + 2I^-$. With excess of iodine the liberated cyanogen partly reacts to give some iodine cyanide: $C_2N_2 + I_2 = 2ICN$.[140,141] Iodine oxidizes ferrocyanides in solution to ferricyanides:

$$2Fe(CN)_6^{4-} + I_2 = 2Fe(CN)_6^{3-} + 2I^-;$$

the reaction is reversible and the concentration equilibrium constant is[142] approximately $2{\cdot}3 \times 10^2$, being greatly dependent on the ionic strength of the solution, the nature of the cations present and the presence of any additional anions.[142-144] The reaction is also photosensitive.[145] With an appreciable excess of iodine, ferrocyanides are themselves oxidized to Prussian blue, iodine cyanide and cyanide ions.[146]

It was demonstrated in 1922 that the reaction between potassium azide and iodine was catalyzed by carbon disulphide: $2KN_3 + I_2 = 2KI + 3N_2$. It was shown that the carbon disulphide is first converted into potassium azido-dithiocarbonate, $KSCSN_3$, which reacts with the iodine to give azido-carbon disulphide $2KSCSN_3 + I_2 = 2KI + (SCSN_3)_2$. This in turn reacts with potassium azide to give potassium azido-dithiocarbonate again and elementary nitrogen, $2KN_3 + (SCSN_3)_2 = 2KSCSN_3 + 3N_2$.[147] It was subsequently shown that many other sulphur compounds similarly catalyze the evolution of nitrogen from the otherwise stable potassium azide-iodine mixture[148] and this reaction has become the basis of a sensitive test for sulphides and sulphur compounds, but not for free sulphur which does not catalyze the reaction.[149] The mechanism of this reaction,[150] its velocity constant and the corresponding data for the analogous reaction involving bromine[151] have been discussed.

Both hydrazine and hydroxylamine, in aqueous solution as their hydrochlorides, are oxidized by iodine, nitrogen and nitrous oxide being formed respectively:[152,153]

$$N_2H_4,2HCl + 2I_2 \rightarrow N_2 + 4HI + 2HCl$$

and

$$2NH_2OH,HCl + 2I_2 \rightarrow N_2O + 4HI + 2HCl + H_2O.$$

The experimentally determined reaction rates agree well with the equations

$$-\frac{d[I]}{dt} = k.\frac{[N_2H_5^+][I_3^-]}{[I^-]^2[H^+]} \text{ and } -\frac{d[I]}{dt} = k.\frac{[NH_2OH,HCl]\ [I_3^-]}{[I^-]^2[H^+]^2},$$

which are based on the assumption that the effective oxidizing agent is hypoiodous acid, HOI.[153]

Iodine reacts quantitatively with lead tetrachloride to form iodine monochloride: $PbCl_4 + I_2 = PbCl_2 + 2ICl$.[154] Iodine is oxidized to iodate by perchlorates,[155,156] chlorates[157] and bromates[158] (see page 874) and by a mixture of aqueous alkali iodide and borate.[159]

Iodine catalyzes the reaction between iron and carbon monoxide giving iron pentacarbonyl: $Fe + 5CO \rightarrow Fe(CO)_5$.[160] The role of iodine as a catalyst in the hydrogen-chlorine reaction,[161] and its effect on the ignition temperatures of hydrocarbon combustion reactions[162] have been discussed. In the hydrogen-oxygen reaction traces of iodine greatly lower the upper explosion limit, shifting the region of self-ignition to higher temperatures.[163]

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SECTION XXXIII

THE PREPARATION OF HYDROGEN IODIDE AND HYDRIODIC ACID

By G. J. HILLS

The principal methods of preparing hydrogen iodide and hydriodic acid remain largely unchanged. The exact experimental details of the catalyzed preparation of hydrogen iodide from gaseous iodine and hydrogen have been described[1] and a diagram of the most recent apparatus used in this method has been given.[1a] Finely divided platinum metal heated to at least 300°C. is recommended for use at normal pressures;[1,2] at higher pressures, moist chromic chloride, heated to 150 – 200°C., has been successfully used.[3] Hydrogen and iodine also combine when subjected to a silent discharge.[4]

In the preparation of hydriodic acid by passing hydrogen sulphide rapidly into a suspension of iodine in water, filtration through sand is suggested as the most effective way of removing the precipitated sulphur.[5] The presence of sulphur in the hydriodic acid solution appears to cause decomposition, particularly when the solution is distilled, and dialysis through a collodion membrane may be necessary to remove colloidal sulphur.[6]

Hydriodic acid can be conveniently prepared on a large scale by the hydrolysis of phosphorus iodides, prepared by heating together iodine and red phosphorus. In order to suppress the formation of explosive hydrides of phosphorus, excess of iodine must be present throughout.[7] On a laboratory scale hydrogen iodide has been prepared by the action of iodine on tetralin.[8] Hydriodic acid solution can be obtained by heating an iodine suspension in water with activated charcoal. The hypoiodous acid produced by hydrolysis of the iodine is reduced by the charcoal:

$$I_2 + H_2O \longrightarrow HI + HOI; \quad 2HOI + C \longrightarrow CO_2 + 2HI.$$

Only dilute solutions of hydriodic acid can be prepared in this way but much higher yields are obtainable by passing a mixture of steam and iodine vapour over activated charcoal at 700 – 800°C.[9]

These methods of preparation have been critically compared by Moles who has described some of the difficulties involved in manipulating gaseous hydrogen iodide. It is decomposed by light, by most organic substances, *e.g.*, tap-grease, and also by large glass surfaces, particularly in the presence of traces of water.[10] Anhydrous hydrogen iodide is conveniently prepared from its aqueous solution by dropping the solution on to phosphorus pentoxide, bubbling the evolved gas through a saturated solution of calcium iodide to remove iodine and finally drying the gas over more phosphorus pentoxide.[11]

Hydrogen iodide is usually stored in aqueous solution, but even as hydriodic acid it is sensitive to light and to impurities, and it should be preserved in a well-stoppered dark glass bottle sealed with paraffin. If the air above the liquid is displaced by some inert gas before the bottle is sealed, the hydriodic acid can be kept in a satisfactory condition for some time.[5] The addition of approximately 0·1% of red phosphorus inhibits the liberation of iodine.[12] Hydrogen iodide and water form a constant-boiling mixture containing 57% HI, and hydriodic acid may therefore be berified by distillation, preferably in an inert atmosphere, the fraction distilling between 125 and

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127°C. being collected.[5] Recommended specifications for hydriodic acid as an analytical reagent have been described.[13]

Syrup of hydriodic acid, a solution of hydrogen iodide and sugar in water, has pharmaceutical uses and is often preferred to iodine as an internal antiseptic. The factors affecting its stability and purity have been studied.[14,15]

Deuterium iodide may be prepared directly from its elements in the manner described above[16,17] but the most convenient method of preparation is to add red phosphorus to a suspension of iodine in heavy water, D_2O.[18] Precautions similar to those described for hydrogen iodide must be exercised in the manipulation and storage of deuterium iodide.

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SECTION XXXIV

THE PHYSICAL AND CHEMICAL PROPERTIES OF HYDROGEN IODIDE AND HYDRIODIC ACID

By G. J. HILLS

THE PHYSICAL PROPERTIES OF HYDROGEN IODIDE

The physicochemical properties of hydrogen iodide, which is a colourless gas at room temperature, have been reviewed by Moles.[1] It shows marked deviations from the ideal gas laws owing, it is suggested, to a significant concentration of dimeric H_2I_2 molecules.[2] The viscosity of gaseous hydrogen iodide at 0°, 20·6°, 100·2° and 250°C. has been determined as 1·839, 1·873, 2·404 and $3{\cdot}178 \times 10^{-4}$ poise respectively.[3,4] Its critical temperature is 424·1°K. (150·9°C.) and its critical pressure 82 atmospheres.[5,6]

At 237·75 ± 0·05°K., (−35·41°C.) hydrogen iodide condenses to a colourless liquid,[7] the vapour pressure of which is given by the equation:[1]

$$\log p_{\text{mm.}} = 7{\cdot}20883 - \frac{1025{\cdot}71}{T} \qquad \text{or, more accurately, by}^{8}$$

$$\log p_{\text{mm.}} = 26{\cdot}119 + 0{\cdot}002293T - 7{\cdot}111 \log T - \frac{1636}{T}$$

Its internal pressure has been calculated as 2131 atmospheres.[9]

At 222·31°K., (−50·85°C.) liquid hydrogen iodide freezes to a colourless solid,[7] the vapour pressure of which is given by the equation:[8]

$$\log p_{\text{mm.}} = 10{\cdot}493 - 0{\cdot}003167\, T - 0{\cdot}377 \log T - \frac{1406}{T}.$$

The crystal structure of the solid has been determined as a tetragonal face-centred lattice,[10] the unit cell containing 4 molecules of HI and being very similar to that of solid xenon.[11] If solid hydrogen iodide is cooled to 15°K., transition points are detected at 125°, 82° and 21°K.[7,10] At 78°K., the density of solid hydrogen iodide was found[12] to be 3·537 g. c.c.$^{-1}$

The heat capacity of hydrogen iodide has been determined from 15°K. to the boiling point. The latent heat of fusion and the latent heat of vaporization were found to be 686·3 ± 0·8 and 4724 ± 5 g.-cal.mole^{-1} respectively. From these data, together with the molar heats of transition, the entropy of gaseous hydrogen iodide at the boiling point was evaluated[7] as 47·8 ± 0·1 g.-cal.deg.$^{-1}$mole^{-1},[13] which is in good agreement with the value of 47·7 g.-cal.deg.$^{-1}$mole^{-1} calculated from spectroscopic data.[14] Its entropy at 25°C., $S^{\circ}_{298{\cdot}16^{\circ}\text{K}}$, is[15] 49·314 g.-cal.deg.$^{-1}$mole^{-1}. The zero-point energy of hydrogen iodide was calculated[16] to be 3258 g.-cal.mole^{-1} and[17] that of the molecular crystal 164 g.-cal.mole.$^{-1}$ The chemical constant of hydrogen iodide, deduced from vapour pressure measurements, is + 0·780.[18] Various empirical relationships have been proposed connecting the entropy of fusion, the heat of vaporization or the boiling point with the atomic structure of hydrogen iodide.[19,20]

The heat of formation of gaseous hydrogen iodide from hydrogen and solid iodine, based on calorimetric investigations of the reaction HI (gas) + $\frac{1}{2}Cl_2$ = HCl (gas) + $\frac{1}{2}I_2$ (solid) at 22°C., was calculated[21,22] to be 5·97 ± 0·05 kg.-cal.mole.$^{-1}$ The most recent value for $\Delta H^{\circ}_{298{\cdot}16^{\circ}\text{K}}$ taken from the tables of the United States National Bureau of Standards is[15] 6·20 kg.-cal.mole^{-1}; the corresponding standard free energy of formation, $\Delta G^\circ_{298.16^\circ\text{K.}}$ is[15] 0·31 kg.-cal. mole^{-1}. The standard heat of formation of HI at 0°K., ΔH°_0, has been calculated[23] as 6·73 kg.-cal mole^{-1}. Values of the heat of formation, the free energy and entropy of formation, the molar heat capacity and the equilibrium constant of formation from 0° to 1500°K. are also given in the tables of thermodynamic data published by the United States National Bureau of Standards.[15] (See page). The H–I bond energy is given[24] as 71·2 kg.-cal.mole^{-1}. The force fields of the hydrogen iodide molecule have been discussed[25,26] and the most recent value for the equilibrium interatomic distance is 1·504 A. From the characteristic vibration frequency of the hydrogen iodide molecule the force constant, corrected for anharmonicity, was calculated to be $2{\cdot}9 \times 10^5$ dynes per cm.[25]

The ionization potential of hydrogen iodide has been determined as 13·0 ± 0·2 e.v.[27,28] and no direct relation between this and the break-down potential has been observed.[29] Its proton affinity at 25°C. has been calculated[30] as −311 ± 2 kg.-cal.mole^{-1}.

The physical properties of deuterium iodide are very similar to those of hydrogen iodide. Solid deuterium iodide, also colourless, has a vapour pressure given by the equation:[8]

$$\log p_{\text{mm.}} = 10{\cdot}505 - 0{\cdot}003167\,T - 0{\cdot}377 \log T - \frac{1406}{T}.$$

Its melting point is 221·23°K. (−51·93°C.) and its latent heat of fusion is[31] 684·3 g.-cal.mole^{-1}. Over its liquid range, deuterium iodide exerts a vapour pressure given by the equation:[8]

$$\log p_{\text{mm.}} = 26{\cdot}129 + 0{\cdot}002293\,T - 7{\cdot}111 \log T - \frac{1636}{T}.$$

Its boiling point at 760 mm., calculated from this equation, is 237·0°K., but later work suggests that a value of 237·25°K. (−35·91°C.) is to be preferred.[31] The latent heat of vaporization of deuterium iodide is[8] 4716 g.-cal. mole^{-1} and its critical temperature[32] is 421·8°K. (148·6°C.) From heat capacity measurements on solid and liquid deuterium iodide, together with the thermal data above, its entropy at 237·25°K. in the gaseous state was computed to be 49·20 g.-cal.deg.$^{-1}$mole^{-1}, which compares well with the statistical value of 49·14.[31] The zero point energy of deuterium iodide has been calculated[16] as 2319·98 g.-cal.mole^{-1}.

The standard heat of formation of gaseous deuterium iodide, $\Delta H^\circ_{298.1^\circ\text{K.}}$, is 1159 ± 15 g.-cal.mole^{-1} and its entropy of fomation, $\Delta S^\circ_{298.1^\circ\text{K}}$, is 1·303 g.-cal.deg.$^{-1}$mole.$^{-1}$ Both values were calculated from spectroscopic data.[33]

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THE PHYSICAL PROPERTIES OF HYDRIODIC ACID

Hydrogen iodide dissolves in many solvents, particularly water and other hydroxy-compounds, to give solutions which are strongly acid. At room temperature, aqueous hydriodic acid solutions are virtually wholly dissociated into hydrogen and iodide ions.[1]

The boiling points of various aqueous hydriodic acid solutions, are given in Table I.

TABLE I. - BOILING POINTS OF AQUEOUS SOLUTIONS OF HYDROGEN IODIDE

Percentage HI W./W.	Boiling point, °C., at 746 mm.
15·1	102
27·3	105
39·0	109
48·0	116
52·5	123·2
54·9	125·8
56·7	126·7
56·8	124
58·0	123
60·0	112
64·9	86

The constant-boiling mixture corresponding to 56·7% HI W./W. is seen to exhibit a maximum boiling point of 126·7°C.[2] The variation of the surface tension of hydriodic acid solutions with composition has also been studied.[3] The results of a refractometric investigation at 25°C. of aqueous hydriodic acid solutions are given in Table II, where $n_{D_3}^{25}$ refers to the yellow D_3 line of helium.[4]

TABLE II. - DENSITY AND REFRACTIVE INDEX OF AQUEOUS SOLUTIONS OF HYDROGEN IODIDE

% HI, W./W.	% HI, W./V.	Density d_4^{25}	Refractive index $n_{D_3}^{25}$	Equivalent refraction $R_{D_3}^{25}$
0	0	0·99707	1·33248	–
1·5741	1·6755	1·14084	1·36395	18·636
2·6176	2·9029	1·23659	1·38497	18·555
4·0012	4·6927	1·36451	1·41322	18·450
6·0440	7·7330	1·55478	1·45529	18·276
7·2184	9·7407	1·66449	1·47963	18·180

Earlier work on the refractive indices of aqueous and alcoholic solutions of hydrogen iodide has been reviewed.[5] The magneto-optical rotation of hydrogen iodide in aqueous solution has been determined[6] as $13{\cdot}44 \times 10^{-10}$ minutes cm^2. Its coefficient of magnetization has been measured by the method of falling drops and both H^+ and I^- were found to be diamagnetic, the susceptibility of the iodide ion being $-49{\cdot}9 \times 10^{-6}$ c.g.s. units.[7]

Aqueous hydriodic acid is a strong electrolyte, the degree of dissociation into ions at normal temperatures being at least 99%.[1] Its mean molal ionic activity coefficients, $\gamma_{\pm}$, and osmotic coefficients, ϕ, between 0·05 and 3M. have been determined isopiestically at 25°C. and are given in Table III.[8,9] These results are in good agreement with those obtained earlier from measurements of the e.m.f. of the cell $H_2|HI(aq)|AgI|Ag$.[10] Using these e.m.f. data and

TABLE III.- MEAN MOLAL IONIC ACTIVITY AND OSMOTIC COEFFICIENTS OF AQUEOUS SOLUTIONS OF HYDROGEN IODIDE

Moles HI per 1000g. H_2O	$\gamma_{\pm}$ HI	Φ HI	Moles HI per 1000g. H_2O	$\gamma_{\pm}$ HI	Φ HI
0·05	0·845	0.956	0·7	0·883	1·057
0·10	0·818	0.953	1·0	0·965	1·116
0·20	0·807	0.969	1·5	1·139	1·216
0·30	0·811	0.984	2·0	1·367	1·323
0·50	0·839	1.019	3·0	2·025	1·543

the more recent activity coefficients, $E^{\circ}_{25^{\circ}C.}$ for this cell was calculated as 0·1517V., and this leads to a value of 0·5352V. for the iodine–iodide electrode, also at 25°C. The value of E° for the above cell has also been obtained directly and the results for various temperatures are given in Table IV.[12]

TABLE IV.- VALUES OF E° FOR THE CELL
H_2 | HI(aq.) | AgI | Ag.

Temp °C.	5	10	15	20
E°v.	0·14712	0·14805	0·14902	0·15062
Temp. °C.	25	30	35	40
E°v.	0·15225	0·15396	0·15583	0·15792

The above activity coefficients lead to a value of 5–5·5 A. for the distance of closest ionic approach depending on the form of the Debye–Hückel expression used.[9] The limiting equivalent conductance of hydriodic acid in aqueous solution at 25°C. has been determined directly and found[12] to be 432·3 $ohms^{-1}$; the corresponding value calculated[13,14] from the most recent limiting ionic conductances for the hydrogen and iodide ions is 426.6 $ohms^{-1}$. The diffusion of hydriodic acid in aqueous solution has also been studied.[15]

The heat of formation and the heat of dilution of aqueous hydrogen iodide have been determined directly; at infinite dilution, the heat of formation at 25°C. was found[16] to be −13·21kg.-cal.$mole^{-1}$ The partial molal heat-capacity of hydriodic acid, $\bar{C}$, has been found to be a linear function of $m^{1/2}$, where m is the molality, over the range $m = 0$ to $m = 3$. It is given by the equation $\bar{C} = \bar{C}^{\circ} + Am^{1/2}$, where at 25°C. $\bar{C}^{\circ} = -33{\cdot}7$g.-cal. and $A = 15{\cdot}9$.[17]

The electrolytic dissociation of hydrogen iodide in non-aqueous solvents has been studied by determining its electrical conductivity.[18-22] In methyl and ethyl alcohols, hydriodic acid is a strong electrolyte,[18,20,21] the equivalent conductances at 25°C. being given respectively by

$$\Lambda_{\mathrm{MeOH}} = 212{\cdot}2 - \frac{98{\cdot}9n}{n+0{\cdot}235} \quad \text{and}$$

$$\Lambda_{\mathrm{EtOH}} = 93{\cdot}2 - \frac{42{\cdot}7n}{n+0{\cdot}0583},$$

where n represents the concentration of hydrogen iodide in g.per litre.[18] Hydrogen iodide in pyridine is a weak electrolyte and its dissociation constant, determined from conductance measurements, was found to be $5{\cdot}9 \times 10^{-4}$g. equivalent $litre^{-1}$ at 25°C.[22]

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THE CHEMICAL PROPERTIES OF HYDROGEN IODIDE AND HYDRIODIC ACID

Hydrogen iodide is unstable at room temperatures and above, slowly decomposing to hydrogen and iodine. At 25°C. the standard free energy change for this decomposition is −0·31 kg.-cal. per mole.[1] The uncatalyzed reaction is slow at normal temperatures but attains a measurable velocity above 400°C. and many determinations have been made of the decomposition rate in the temperature range 550 – 800°C., particularly by Bodenstein[2] and his collaborators and by Hinshelwood.[3] The homogeneous decomposition is bimolecular, the velocity constant, k, being given by the equation:

$$\log k = -\frac{10030}{T} + 0{\cdot}5 \log T + 13{\cdot}001,$$

where T is the absolute temperature.[4] This leads to an activation energy of 45·9 kg.-cal.mole^{-1} which is in reasonable agreement with most previous experimental values[2,3,5] and with the value calculated from statistical mechanics.[6-8] The mutual interaction between hydrogen iodide molecules as a preliminary to reaction has been considered in detail.[9-11] The influence of water vapour on the decomposition reaction was found to be very small.[12]

The decomposition of hydrogen iodide is catalyzed at metal surfaces such as gold[3] and platinum;[13] the reaction is then of zero order with an activation energy of 25 kg.-cal. per mole[3] and is probably a simple monomolecular decomposition of adsorbed hydrogen iodide molecules to adsorbed hydrogen and iodine atoms.[13-15]

Deuterium iodide also decomposes in a similar way, the velocity constant of the homogeneous reaction over the temperature range 696° – 779°C. being given by the equation:[4]

$$\log k = -\frac{10150}{T} + 0{\cdot}5 \log T + 12{\cdot}914.$$

This corresponds to an activation energy of 46·6 kg.-cal.mole^{-1} which, like that of hydrogen iodide, is in reasonable agreement with the value calculated by statistical mechanics.[6-8]

The equilibrium constant, K, for the exchange $HI + D_2 \rightleftharpoons DI + H_2$ has been determined[16-18] and is given by:-

$$\ln k = \ln 2{\cdot}412 - \frac{60{\cdot}44}{T}.$$

The ortho-para hydrogen conversion which takes place in an equilibrium mixture of gaseous hydrogen iodide, iodine and hydrogen[19] has been shown to be partly due to direct exchange of the hydrogen with the hydrogen iodide, $HI + H_2(\text{para}) \rightarrow HI + H_2(\text{ortho})$.[20] This reaction is in addition to the reactions

$$H_2(\text{para}) + I_2 \rightarrow 2HI \text{ and } 2HI \rightarrow H_2(\text{ortho}) + I_2$$

and almost certainly accounts for the large temperature-dependence of this conversion reaction.[20]

The decomposition of hydrogen and deuterium iodides is also catalyzed by light.[21-26] The mechanism of the photo-decomposition is probably (1) $HI + h\nu \rightarrow H + I$; (2) $H + HI \rightarrow H_2 + I$; (3) $I + I \rightarrow I_2$, in accord with the quantum efficiency of the reaction which is approximately 2.[26,27] A bimolecular reaction between an activated and an unactivated molecule, which has been suggested, is therefore unlikely.[26] When solid hydrogen iodide is photochemically decomposed at low temperatures (< 100°K.), it is found that para-hydrogen is preferentially formed, owing, it is suggested, to the paramagnetic action of free iodine atoms.[28] A later attempt to repeat this work was not successful.[29] A mechanism similar to that outlined above has been shown to operate in the photolysis of hydrogen iodide in aqueous solution

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and in hexane solution.[30] The effect of various inorganic salts on the stability of aqueous hydriodic acid has been studied in detail. Most salts markedly accelerate the decomposition although some such as those of alkaline earths, zinc and cadmium retard the decomposition.[31] The decomposition of gaseous hydrogen iodide is accelerated by *X*-radiation[32] and by active nitrogen.[33,34]

The reaction between hydrogen iodide and oxygen is also sensitive to light.[35,36] The primary step in the photochemical oxidation is again the dissociation by a photon of a hydrogen iodide molecule into a hydrogen atom and an iodine atom, and the ensuing reaction path is almost certainly (1) $H + HI \rightarrow H_2 + I$; (2) $H + O_2 \rightarrow HO_2$; (3) $HO_2 + HI \rightarrow H_2O_2 + I$; (4) $I + I \rightarrow I_2$. As in the hydrogen-oxygen reaction, HO_2 plays a vital part in the mechanism, and it has been suggested that its reaction with a hydrogen iodide molecule, although represented here by a simple binary step, may involve a three-body collision probably involving another oxygen molecule.[36,37] The influence of the wave-length of the incident radiation has been investigated in some detail, but with apparently inconclusive results.[38-40] Deuterium iodide is photochemically oxidized faster than hydrogen iodide but the mechanism is almost certainly the same.[41] Hydriodic acid is also photochemically oxidized in aqueous solution.[42-47] In the dark, the reaction is not accelerated by ozone.[48] The velocity of the oxidation of hydriodic acid with hydrogen peroxide has been shown to be 1·4 times the rate of the corresponding deuterium reaction, $D_2O_2 + 2DI \rightarrow I_2 + 2D_2O$.[9]

The reaction between chlorine and hydrogen iodide is very fast. In carbon tetrachloride solution it has been shown to be bimolecular, proceeding in two stages, (1) $Cl_2 + HI \rightarrow ICl + HCl$, and (2) $ICl + HI \rightarrow HCl + I_2$. The reaction is too fast to be accounted for by the mechanism $2HI + Cl_2 \rightarrow 2HCl + I_2$ and the high velocity is not due to traces of moisture or to a surface reaction. The half-life period of the reaction at -110°C. is only 0·2 sec. and an activation energy of less than 5·5 kg.-cal.mole^{-1} is indicated.[50] Cyanogen chloride and bromide react by a similar two-stage mechanism, i.e., (1) $BrCN + HI \rightarrow HBr + ICN$, (2) $ICN + HI \rightarrow HCN + I_2$.[51] The addition reaction between hydrogen iodide and hydrogen bromide has been studied magnetochemically.[52]

Hydriodic acid reacts quantitatively with iodic acid to give iodine, $5HI + HIO_3 = 3H_2O + 3I_2$. The kinetics of this reaction,[53,54] the exact conditions under which it goes to completion and the subsequent titration of the iodine with thiosulphate solutions have all been investigated.[55] Further details of this reaction are given in the section dealing with iodates (see page 880). Hydriodic acid is similarly rapidly oxidized by bromic acid and deuterium iodide is oxidized even faster.[56]

Small concentrations of hydriodic acid reduce concentrated sulphuric acid to sulphurous acid; high concentrations reduce it to hydrogen sulphide.[57,58] In dilute sulphuric acid solution, both sulphurous acid and hydrogen sulphide reduce iodine to hydriodic acid and the limiting acid concentration above which this reaction is reversed is approximately 50%.[57] Thiosulphurous acid is reduced to sulphur by hydriodic acid: $H_2S_2O_2 + 2HI = 2H_2O + 2S + I_2$.[59]

The reaction between hydriodic acid and nitric acid is represented formally by the equation, $HNO_3 + 2HI = HNO_2 + I_2 + H_2O$. The proposed mechanism of the reaction involves the presence of a catalytic amount of nitrous acid and is in five stages: (1) $HNO_2 + HNO_3 \rightleftharpoons N_2O_4 + H_2O$; (2) $N_2O_4 \rightleftharpoons 2NO_2$; (3) $NO_2 + I^- \rightleftharpoons NO_2^- + I$; (4) $NO_2^- + H^+ \rightleftharpoons HNO_2$; (5) $I + I \rightleftharpoons I_2$. The first step is rate-determining and has[60] a velocity constant at 25°C. of between 0·8 and 1·6 litre^{2}mole^{-2}min^{-1}. Excess hydriodic acid reduces the nitrous acid to nitric oxide, $2HNO_2 + 2HI = 2NO + I_2 + H_2O$,[60,61] and possibly even to nitrogen.[62]

The kinetics of the reactions between hydriodic acid and chromic acid, chromates and dichromates have been investigated and the effect of many inorganic chlorides, nitrates and sulphates on the reaction velocity noted.[63,64] In acid solution the reaction is very fast, and in volumetric titrations involving the liberation of iodine by chromic acid a low pH is recommended. It has however been pointed out that this increases the possibility of oxidation of hydrogen iodide and that since the reaction is catalyzed by oxalate ions, and to a lesser degree by citrate and tartrate ions, lower acid concentrations can just as easily be used if such ions are present.[65] Vanadic acid is readily reduced by hydriodic acid to vanadium tetroxide: $V_2O_5 + 2HI = V_2O_4 + I + H_2O$.[66,67] Arsenic acid is reduced only in strongly acid solution.[68] In the presence of potassium persulphate, a mixture of hydriodic acid and silver nitrate, is oxidized to Ag_3IO_5.[69]

Hydriodic acid has been shown to corrode many metals and alloys but this can be prevented in the case of steels by the introduction of molybdenum or tungsten into the alloy.[70] In concentrated hydriodic acid, cobalt ions give a bright green coloration and nickel ions a blood-red coloration. The absorption spectra of both solutions have been studied, and it is suggested that the intense colours are due to complex compounds of the type MI_3H.[71]

Many sparingly soluble compounds are more soluble in hydriodic acid solutions than in hydrochloric or hydrobromic acid solutions of similar strength.[72] In the case of the alkaline earth sulphates, lead sulphate and chromium sulphate, some of the sulphate is reduced to hydrogen sulphide and iodine is liberated.[73] Stannic oxide dissolves readily in boiling hydriodic acid, the tetra-iodide being formed: $SnO_2 + 4HI = SnI_4 + 2H_2O$.[74]

Nitrogen iodide reacts with excess of aqueous hydriodic acid to form ammonium iodide and hydrogen tri-iodide: $2NH_3NI_3 + 5HI = 2NH_4I + HI_3$. The reaction is quantitative and has a heat of reaction at 19°C., ΔH, equal to $-58{\cdot}0 \pm 1{\cdot}3$ kg.-cal.mole^{-1}, from which the heat of formation of ammonium iodide from its elements at 19°C. is calculated to be -35 kg.-cal.mole^{-1}.[75]

A mixture of phosphorus and hydrogen iodide is a powerful reducing agent. Phosphonium iodide is formed in the reaction and is the actual reducing agent. Since its oxidation products include hydriodic acid, it appears that this acid functions merely as a catalyst in what is essentially a reduction by elementary phosphorus.[76]

Hydrogen iodide is strongly adsorbed on glass surfaces.[77] Its adsorption on silica gel has been measured over the temperature range −45°C. to +60°C and found to be approximately the same as for hydrochloric and hydrobromic acids.[78] Hydrogen iodide is adsorbed on silver iodide.[79] The theory of adsorption of hydrogen iodide molecules on graphite has been discussed in terms of the Brunauer–Emmett–Teller multilayer adsorption theory.[80]

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SECTION XXXV

THE OXIDES AND OXY-ACIDS OF IODINE.

By G. J. HILLS

HYPOIODOUS ACID AND THE HYPOIODITES

The addition of iodine to aqueous alkali hydroxide solutions remains the principal method of preparing alkali hypoiodites, and from these other metallic hypoiodites or solutions of the free acid can be obtained (Mellor, II, 267-280) Hypoiodous acid can also be prepared by adding iodine to an aqueous solution of silver acetate; $I_2 + H_2O + AgOAc = HOI + AcOH + AgI$. The precipitation of the silver iodide effectively completes the hydrolysis of the iodine.[1]

Hypoiodous acid solutions are unstable and decompose forming hydriodic acid and oxygen; $2HOI = 2HI + O_2$. Since the reaction, $HOI + HI \rightleftharpoons H_2O + I_2$, is reversible and since hydriodic acid is in any case readily oxidized by atmospheric oxygen, solutions of hypoiodous acid always contain free iodine. The decomposition of hypoiodous acid has been shown to be of second order with respect to its concentration and, in the presence of silver salts at least, to involve the possible formation of iodous acid, HIO_2:[2,2a]

$$\begin{aligned} AgOAc + 2HOI &\rightarrow HIO_2 + AgI + HOAc; \\ HIO_2 &\rightarrow HI + O_2. \end{aligned}$$

The decomposition is accelerated by the presence of charcoal.[3]

In alkaline solution the decomposition is that of the hypoiodite ion, three such ions interacting to form an iodate ion;[4,5] $3OI^- \rightarrow IO_3 + 2I^-$. The rate of this transformation has been measured, the concentration of hypoiodite being determined at various time intervals using its rapid reaction with phenol and tyrosine[5] or with hydrazine sulphate and hydrogen peroxide.[4] In strongly alkaline solutions at 25°C., the rate is given by[5]

$$-d[OI^-]/dt = 2{\cdot}9[OI^-]^2 + 104[OI^-]^2.[I^-]/[OH^-].$$

Hypoiodous acid is a very weak acid,[6] its dissociation constant at 20°C., determined analytically,[7] being $4{\cdot}5 \times 10^{-13}$ g.ions litre^{-1}. In organic preparative work it is frequently used as an oxidizing agent[8-9b] and also as an iodinating agent.[10,10b]

IODINE TRIOXIDE AND IODOUS ACID

Although di-iodine dioxide, I_2O_2, has been thought to be an intermediate in the oxidation of iodine,[11] iodine trioxide, I_2O_3, is the lowest oxidation state of iodine the existence of which is known with certainty (Mellor, II, 285). Iodine trioxide is not known in the free state but it can be isolated as the yellow sulphate, I_2O_3,SO_3. This can be prepared by shaking together 2 moles of iodine and 3 moles of iodine pentoxide in cold concentrated sulphuric acid. The sulphate is insoluble and the yield is quantitative:

$$2I_2 + 3I_2O_5 + 5H_2SO_4 \rightarrow 5I_2O_3,SO_3 + 5H_2O.$$

It can also be prepared by prolonged heating of a solution of iodine pentoxide or iodic acid in fuming sulphuric acid:[12-14]

$$I_2O_5 + H_2SO_4 \rightarrow I_2O_3,SO_3 + H_2O + O_2.$$

Attempts to repeat Chrétien's preparation of the hemihydrate, $I_2O_3,SO_3,\frac{1}{2}H_2O$, have not been successful,[12,13,15] but from oleum solution a white crystalline material having the formula $I_2O_3,4SO_3,H_2O$ is obtained.[13]

The acid corresponding to iodine trioxide, iodous acid, HIO_2, has not been isolated. It has been suggested that a solution of iodous acid is formed by adding silver nitrate to a solution of iodine in aqueous potassium iodide. After standing, the solution is filtered from precipitated silver iodide and, it is claimed, contains an appreciable concentration of iodous acid.[16] The silver salt of this acid, $AgIO_2$, has been characterized and its standard entropy determined as 34·2 ± 0·8 g.-cal.deg.$^{-1}$mole^{-1}.[17]

IODINE TETROXIDE

Partington and Bahl have re-examined much of the earlier work on the preparation of this oxide.[15] They found that it is not formed by the action of concentrated nitric acid on iodine although it may well be an intermediate in this reaction.[18] The Muir–Millon method of preparation was employed (Mellor, II, 291) and yellow granular iodine tetroxide was obtained in this way. This compound is not hygroscopic and is only slightly soluble in cold water. It dissolves in hot water forming iodic acid and iodine. With hydrochloric acid, chlorine is evolved and iodine monochloride is formed: $I_2O_4 + 8HCl = 2ICl + 3Cl_2 + 4H_2O$.[15]

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THE PREPARATION OF IODINE PENTOXIDE

The thermal dehydration of iodic acid remains the most satisfactory method of preparing iodine pentoxide. At 70°C., the hydrate $3I_2O_5,H_2O$ is readily formed but the temperature must be raised to 200°C. before further loss of water occurs and complete dehydration takes place. Above 275°C. iodine pentoxide itself decomposes into iodine and oxygen.[1-5] Since the synthesis of iodine pentoxide is one method of determining the atomic weight of iodine, the factors affecting the purity and stoicheiometry of the oxide have been investigated in some detail.[6-10] Very pure iodine pentoxide is prepared by first oxidizing pure iodine to potassium iodate with recrystallized potassium permanganate. Barium iodate is then precipitated and converted into iodic acid by treatment with sulphuric acid. The iodic acid is repeatedly crystallized in platinum apparatus and traces of barium sulphate are removed by filtration through platinum sponge. The final crop of crystalline iodic acid, which is almost odourless, is then placed in a platinum boat and dehydrated in a stream of pure air at 200°C.

Iodine pentoxide can also be prepared by the photo-oxidation of several organic iodo-compounds such as methylene iodide, iodoform and carbon tetraiodide. Using ultra-violet irradiation, a high yield is obtained from methylene iodide and it is suggested that the oxidation has the following mechanism: $CH_2I_2 + O_2 \rightarrow CH_2I_2O_2$; $CH_2I_2O_2 \rightarrow HCHO + I_2O$; $I_2O + 2O_2 \rightarrow I_2O_5$.[11]

THE PROPERTIES OF IODINE PENTOXIDE

Iodine pentoxide is a white crystalline compound of density 5·1 ± 0·1.[4,9,10] The most recent value for its standard free energy of formation is -42·34 kg.-cal.mole^{-1} at 25°C.[12]

Iodine pentoxide reacts with water and two hydrates are known: I_2O_5,H_2O, corresponding to iodic acid, and $3I_2O_5,H_2O$. The corresponding heats of hydration are 2096 and 1159 kg.-cal.mole^{-1} respectively.[1] The existence of $2I_2O_5,H_2O$ has not been confirmed.[1] $3I_2O_5,H_2O$ can be recrystallized from 60% nitric acid[2] and forms colourless, holohedral, monoclinic crystals the unit cell of which has *a:b:c* ratios of 0·901:1:0·891 and β = 112°53′. Its density is 4·734.[3] Iodine pentoxide dissolves in dilute mineral acids, forming iodic acid, but the solubility steadily decreases with increasing concentration of the solvent acid.[13,14]

Iodine pentoxide reacts with nitric oxide at 120°C. to form iodine and dinitrogen pentoxide: $10NO + 3I_2O_5 \rightarrow 3I_2 + 5N_2O_5$.[15] The amide of iodic acid can be prepared by adding iodine pentoxide to a solution of sodamide in liquid ammonia: $NaNH_2 + I_2O_5 = Na(NH_2I_2O_5)$. By adding dilute sulphuric acid to this sodium salt the free amido-iodic acid is produced, but this decomposes quite rapidly to iodic acid and ammonia.[16]

Iodine pentoxide dissolves in liquid hydrofluoric acid but does not react with it. If this solution is evaporated, unstable solvates of the type I_2O_5,xHF are obtained, but they rapidly regenerate the iodine pentoxide.[17] Bromine trifluoride, however, readily reacts with iodine pentoxide; oxygen is evolved and bromine and iodine trifluoride are formed: $2I_2O_5 + 4BrF_3 = 5O_2 + 2Br_2 + 2IF_3$.[18]

Iodine pentoxide is one of the few compounds that react with carbon monoxide. The reaction, $I_2O_5 + 5CO = 5CO_2 + I_2$, is quantitative and is used to determine carbon monoxide in the atmosphere and in other gaseous systems.[19-22] The temperature at which the determination is carried out is not critical but the gas containing carbon monoxide must be passed very slowly over the solid iodine pentoxide.[23] Methane, chlorine, carbon tetrachloride, phosgene, sulphur dioxide and nitrogen peroxide do not interfere.[24]

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THE PREPARATION OF IODIC ACID

The oxidation of iodine with fuming nitric acid remains the most convenient way of preparing very pure iodic acid.[1] Pure anhydrous iodic acid crystallizes from dilute or semi-concentrated nitric acid (5N.) but from stronger acid the compound $3I_2O_5,H_2O$ separates.[2] (See page 849 and Mellor, II, 293-4)

The oxidation of aqueous iodine solutions by chlorates[3,4] and bromates[5] has been further investigated. The reaction is accelerated by the presence of hydrochloric acid or hydrobromic acid, the liberated chlorine or bromine being very effective in oxidizing the iodine, probably through the intermediate formation of the corresponding iodine monohalide.[3,4] Iodic acid is also formed by the anodic oxidation at a platinum electrode of iodine dissolved in hydrochloric acid.[6] The formation of iodate from alkali hypoiodite solutions has been further discussed,[7] the rate equation being that given on page 870.

Iodine in aqueous suspension is oxidized to iodic acid by silver nitrate. The hydrolysis of the iodine to hydriodic acid and hypoiodous acid is completed by the precipitation of the iodide: $AgNO_3 + I_2 + H_2O \rightarrow AgI + HOI + HNO_3$. The hypoiodous acid then undergoes auto-oxidation to iodic acid and hydriodic acid, and this reaction appears to be catalyzed by silver ions.[8] A description of commercial iodic acid and the probable extent of impurities has been given in the form of a monograph.[9]

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THE PHYSICAL PROPERTIES OF IODIC ACID AND THE IODATES GENERALLY

Relatively few physical properties of solid iodic acid have been studied. The crystal structure of the normal α-modification has been shown to be orthorhombic with 4 molecules of HIO_3 in the unit cell,[1,2] the dimensions of which in Angstrom units are given by:[2]

$$a_0 = 5{\cdot}520 \pm 0{\cdot}005,$$
$$b_0 = 5{\cdot}855 \pm 0{\cdot}005,$$
$$c_0 = 7{\cdot}715 \pm 0{\cdot}005.$$

The space group is $D_2^4 — P_{2_12_12_1}$.

The structure is an aggregate of iodic acid molecules held together by hydrogen bonds and weak I–O bonds.[2,3] In studying the *X*-ray absorption of iodic acid, some reduction of the acid was observed.[4] Its molar volume at 0°K. has been calculated to be 36·1 c.c.[5] Bridgman has measured the compressibility of single crystals of iodic acid,[6] and the change in relative volume with applied pressure is shown in Table I.

TABLE I. - COMPRESSIBILITY OF IODIC ACID

Pressure kg.cm^{-2}	Relative Volume	Pressure kg.cm^{-2}	Relative Volume
0	1·00000	15000	0·94382
2500	0·98900	20000	0·92942
5000	0·97880	25000	0·91534
10000	0·96070	30000	0·90482

Crystalline iodic acid rotates the plane of polarized light, and for the wavelengths 5790, 5460 and 4360 A., the specific rotatory power in degrees.mm.$^{-1}$ is 50·5, 58·7 and 74·5 respectively.[7] Iodic acid has also been shown to be piezo-electric.[8] The molar diamagnetic susceptibility of the iodate ion has been measured.[9,10] The most recent values for the ion in the solid state and in solution are $-47{\cdot}3 \times 10^{-6}$ and $-41{\cdot}4 \times 10^{-6}$ c.g.s. units respectively.[10] A method for computing the entropy of iodic acid has been proposed.[11]

Iodic acid is readily soluble in water. It is not completely ionized at finite concentrations and several values for the dissociation constant of iodic acid in aqueous solution have been recorded:[12-16] 0·26 mole litre^{-1} was obtained by a freezing point method,[13] 0·19 from conductivity measurements[13] and 0·164 from potentiometric measurements.[14] The most recent value, 0·1668 ± 0·0005 mole litre^{-1}, was obtained by an optical method using α-dinitrophenol as indicator.[15] The degree of dissociation decreases with increasing temperature.[17] There also seems little doubt that the undissociated iodic acid molecules polymerize in solution and that a quasi-crystalline structure is present even at low concentrations:[18-22] HIO_3 and $[HIO_3]_2$ are probably the predominant species,[20,21] although the existence of $[HIO_3]_3$ in concentrated solutions has been reported.[21,22] A study of various properties of iodic acid solutions as a function of concentration indicates that changes in the constitution of the solution occur at 0·1 N. and 0·04 N., corresponding, it is suggested, to the change from the trimeric form to the dimeric form and from the dimeric form to the monomeric form respectively.[21,22] The iodate ion is also thought to exist in solution partially in the dimeric form, $I_2O_6^{--}$.[23]

The density, surface tension, viscosity and electrical conductivity of aqueous iodic acid solutions at 20° and 30°C. over a wide concentration range have been determined,[21,22,24] and some of the results for 30°C. are given in Table II.

TABLE II. - DENSITY, SURFACE TENSION, VISCOSITY AND EQUIVALENT CONDUCTIVITY OF AQUEOUS SOLUTIONS OF IODIC ACID.

Concentration mole litre^{-1}.	Density, relative to water at 30°C.	Surface tension, dyne cm.$^{-1}$	Viscosity, poise.	Equivalent conductivity.
0·01	1·00152	71·355	0·0080473	388·6
0·02	1·00310	70·772	80177	366·25
0·04	1·00610	71·210	80599	342·0
0·05	1·00750*	–	–	333·9
0·10	1·01515	71·060	82073	296·25
0·20	1·02990	71·489	83631	259·8
0·40	1·05940	71·540	87188	215·66
0·60	1·08950	71·990	90708	192·6
0·80	1·11815	72·009	94426	175·5
1·00	1·14720	72·609	98422	162·8
2·00	1·29115	72·279	0·0125175	122·83
5·00	1·7128*	–	–	–

(* these values are in g. c.c.$^{-1}$)

The refractive index, parachor, rheochor,[19] Raman spectrum[20-22] and ultraviolet absorption spectrum[25] of iodic acid solutions have also been studied, and the results from some of these studies are shown in Table III.

TABLE III. - REFRACTIVE INDEX, PARACHOR AND RHEOCHOR OF AQUEOUS SOLUTIONS OF IODIC ACID.

Concentration mole litre^{-1}	Refractive Index.	Parachor.	Rheochor.
0	1·331754	–	–
0·01	1·332062	52·315	9·8513
0·02	1·332370	52·380	9·8483
0·05	1·333070	–	–
0·10	1·334163	52·890	9·9366
0·20	1·336454	52·435	9·9160
0·40	1·340966	52·575	9·9930
0·60	1·345610	52·745	10·065
0·80	1·350004	52·913	10·141
1·00	1·354573	53·165	10·221

From the density and refractive index data, the polarizability of the iodate ion was found to be 6·185 × 10^{-24} cm.^{5}, from which the radius of the solvated iodate ion was calculated to be 2·12 A.[26] On the assumption that the ammonium ion and the chloride ion have the same hydrated volume, the apparent molar volume of iodate ion in solution has been evaluated as 25·1 c.c. g.-equivalent^{-1}, which leads to the value for the ionic radius of 2·13 A.[27] The ionic radius obtained from the heat of hydration is 1·82 A.[28] The specific heat capacities at constant pressure of iodic acid solutions have been determined at 25°C.[29] and these, with the corresponding partial molal heat capacity of iodic acid, C_p, are given in Table IV. (See page 877).

From the absolute entropy of potassium iodate, the entropy of the iodate ion in 1M. solution at 25°C. is calculated to be 29·6 ± 1·0 g.-cal.mole^{-1}degree^{-1}.[30]

TABLE IV.- SPECIFIC HEAT AND PARTIAL MOLAL HEAT CAPACITY OF AQUEOUS SOLUTIONS OF POTASSIUM IODATE

Molality of KIO_3.	Specific heat.	$\bar{C}_p$
0	0.99780	−36.95
0.05	0.99677	−13.73
0.10	0.99629	− 6.10
0.20	0.99629	+ 3.85
0.50	0.99952	17.89
1.00	1.01231	29.10
2.00	1.04663	39.29
3.00	1.08812	42.54

Several determinations have been made of the diamagnetic susceptibility of aqueous solutions of iodic acid and iodates.[31–35] Values of $\chi_{\text{ion}} = -52{\cdot}2$,[31] $-51{\cdot}4$[34] and $-46{\cdot}80$[35] e.s.u. have been obtained, the last being the most recent.

The electrical conductivity of iodic acid and iodates has been studied by several workers.[13,36–40] The most recent value[42] for the limiting equivalent conductance of the iodate ion at 25°C. is 40·75 $\text{ohm}^{-1}\text{cm.}^2\text{mole}^{-1}$ which was obtained by extrapolating careful measurements of the conductivity of potassium iodate solutions at low concentrations using Owen's method.[43] Using the accepted value for the limiting ionic conductance of the hydrogen ion[44] the limiting equivalent conductance of iodic acid at 25°C. is therefore 390·6 ohm^{-1} $\text{cm.}^2\text{mole}^{-1}$. The conductivity of iodic acid in anhydrous methanol and ethanol has also been measured. Iodic acid is a very weak acid in these solvents, its dissociation constant in methanol being only 10^{-8} g.-equivalent litre^{-1}.[45]

Both the silver–silver iodate and the mercury–mercurous iodate electrodes are highly reproducible in neutral iodate solutions but not in iodic acid solutions where chemical oxidation of both metals takes place. Measured against a standard calomel half-cell, the standard potential of the silver–silver iodate electrode on the hydrogen scale has been found to be 0·3569 V.[46] and, more recently, 0·3578 V.[47] The solubility product of silver iodate at 25°C. has been determined independently as $3{\cdot}055 \times 10^{-8}$ g. $\text{equivalent}^2\,\text{litre}^{-2}$ and this, combined with the standard potential of the silver–silver ion electrode, gives a value of 0·3551V. for the silver–silver iodate electrode.[14] From measurements of the solubility of silver iodate in nitric acid solutions, the thermodynamic dissociation constant of iodic acid is calculated to be 0·164 g.-equivalent litre^{-1}.[14] The standard potential of the mercury–mercurous iodate electrode at 25°C. was found to be 0·3942 V., from which the solubility product of mercurous iodate is calculated as $1{\cdot}94 \times 10^{-14}$ g. $\text{equivalent}^3\,\text{litre}^{-3}$.[48] Using both electrodes, the activity coefficients of iodates have been studied.[14,48] The standard iodine–iodate oxidation-reduction potential at 25°C. measured at a platinized platinum electrode is + 1·195 ± 0·002 V. From this, the calculated standard free energy of formation of the iodate ion, $\Delta G^\circ_{298.16^\circ\text{K.}}$, is −32,251 g.-cal.g.$\text{ion}^{-1}$ and the standard heat of formation, $\Delta H^\circ_{298.16^\circ\text{K.}}$, −54,966 g.-cal. g.$\text{ion}^{-1}$.[49] No exchange of the iodine between iodide and iodate ions has been detected[50] but it has been claimed that exchange between molecular iodine and iodate ions does occur.[51] The distribution of iodate ions across a 'permselective' membrane (i.e., a membrane selective in its permeability to ions) has also been studied.[52]

The reduction of iodate ions at a dropping-mercury electrode has been shown to be irreversible.[53] The half-wave potential is very sensitive to the nature of the supporting electrolyte and for a 0·001 N. solution of iodate in 0·1 N solutions of various electrolytes has the following values: with univalent cations −1·09v., with bivalent cations −0·84v. and with trivalent cations −0·40v. In acid solution, a value of +0·13v. is obtained.[54] In 0·5 M-sodium fluoride solution, the half-wave potential of the iodate ions is dependent on the pH of the solution. At pH 4·6 or lower, a single half-wave potential of −0·6v. is obtained but at pH 5·8 and above, a single wave occurs at −1·30v. At intermediate pH values, both waves are present, their intensity varying with the pH.[55] A number of equations have been proposed connecting the current density and the potential of the dropping-mercury electrode with the concentration of iodate ions and it has been suggested that the reducible entities are ion pairs of the type $Na_2IO_3^+$, $CaIO_3^+$ etc.[56] The diffusion coefficient for the iodate ion has been determined[57] as $1{\cdot}05 \times 10^{-5}$ $cm.^2 sec.^{-1}$ which is in good agreement with the value calculated on the basis of Davtyan's equation.[58]

The solubility of iodic acid in nitric acid solutions of varying concentrations at 25°C. has been determined[59] and is illustrated in Table V.

TABLE V.- SOLUBILITY OF IODIC ACID IN AQUEOUS NITRIC ACID

% W/W HNO_3	% W/W HIO_3	% W/W HNO_3	% W/W HIO_3
20·23	35·09	50·71	5·74
28·00	21·84	58·66	3·25
35·28	15·20	65·30	1·40
43·32	10·08		

The viscosities of these solutions pass through a minimum which indicates the possible formation of the additive compound $3HNO_3,HIO_3$.[59] Investigations of the solubility relations of the system iodic acid–potassium iodate–water have been extended to cover the temperature range 0 – 50°C. The results indicate that potassium bi-iodate can be recrystallized from aqueous solution although care should be exercised in drying it. Thermal dehydration readily occurs and at 105°C. it is slow but complete. Recrystallized potassium bi-iodate is best washed with alcohol and air-dried.[60]

The adsorption of iodate ions on charcoal is in accord with the Freundlich equation, *n* being equal to unity.[61] The relative adsorption of iodate, bromate and nitrate ions on aluminium, chromium[62] and vanadium hydroxide[63] precipitates has also been studied.

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THE CHEMICAL PROPERTIES OF IODIC ACID AND THE IODATES GENERALLY

Iodates are stable at room temperatures but lose oxygen on heating. The thermal decomposition of added potassium iodate in various baking processes has been investigated using radioactive iodine, ^{131}I; under ordinary baking conditions, there was complete decomposition but no loss of iodine.[1] Potassium iodate is also decomposed when subjected to an electrodeless discharge, and in this case free iodine is produced, together with some potassium iodide and oxygen.[2,3] In neutral aqueous solution potassium iodate is quantitatively reduced to potassium iodide by hydrogen in the presence of active platinum.[4]

The well known reaction between iodic acid and hydriodic acid has been shown[5] to be instantaneous and quantitative even at 0°C.: $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$. A potentiometric study of this reaction has indicated that, to maintain the necessary low pH value, the use of sulphuric acid rather than hydrochloric acid is to be preferred in order to avoid the possible formation of iodine monochloride.[6] Activated charcoal has been shown to inhibit the reaction owing, it is suggested, to preferential adsorption of significant quantities of hydriodic acid.[7] Iodate and bromide ions in acid solution do not react appreciably at room temperature and the equilibrium constant of the reaction:

$$2IO_3^- + 10Br^- + 12H^+ \rightleftharpoons I_2 + 5Br_2 + 6H_2O,$$

at 25°C. is[8] only $1{\cdot}6 \times 10^{-22}$. The mechanism of this reaction,[9] of the corresponding reaction involving chloride ions[9] and also of the normal iodide–iodate reaction[10] has been discussed. Iodic acid is oxidized by fluorine to periodic acid although there is some simultaneous reduction of this product by hydrogen peroxide, also produced in the reaction.[11] In acid solution iodates also are rapidly reduced by hydrogen peroxide.[12]

Further study has been made of the reaction between iodic acid and sulphurous acid, i.e., Landolt's reaction.[13-21] The three consecutive reactions:

$$\text{(i)}\quad IO_3^- + 3SO_3^{--} \rightarrow I^- + 3SO_4^{--},$$

$$\text{(ii)}\quad 5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O,$$

$$\text{(iii)}\quad 3I_2 + 3SO_3^{--} + 3H_2O \rightarrow 6I^- + 6H^+ + 3SO_4^{--},$$

which give rise to the periodic appearance and disappearance of iodine, have been studied separately and the effect of added salts noted.[22,23] Both chloride and bromide ions accelerate the overall reaction[24,25] and step (ii) is certainly catalyzed by thiosulphates.[26,27] Numerous equations connecting the reaction velocity with the concentrations of sulphite and iodate have been proposed but no simple analysis of the kinetics of this reaction has yet emerged. The overall reaction has been shown to be faster in heavy water, D_2O, than in ordinary water.[28]

In acid solution, iodates are reduced by thiosulphates:[29-31]

$$IO_3^- + 6H^+ + 6S_2O_3^{--} \rightarrow I^- + 3S_4O_6^{--} + 3H_2O.$$

This reaction is quantitative and is a useful method of standardizing dilute acids by using them to titrate a known weight of potassium iodate in the presence of excess of sodium thiosulphate, using an ordinary acid-base indicator to detect the first excess of acid. At low hydrogen ion concentrations, the reaction rate is given by

$$-dx/dt = k[IO_3^-][S_2O_3^{--}]^2[H^+]^2$$

where k, the velocity constant, is equal to 3×10^{10} at room temperatures.[32] Mixtures of sulphur and solid iodates do not ignite when treated with concentrated sulphuric acid.[33] Carbon monoxide is quantitatively oxidized by a solution of iodic acid in aqueous sulphuric acid.[34]

Iodic acid oxidizes nitrous acid to nitric acid:

$$3HNO_2 + IO_3^- \rightarrow 3NO_3^- + I^- + 3H^+.$$

The reaction velocity is given by the equation:

$$-dx/dt = \{k_1 + k_2[IO_3^-][H^+]\}\{[IO_3^-][HNO_2]\},$$

from which it is concluded that undissociated nitrous acid and not nitrite ion is the reducing species in this reaction.[35] Hypophosphites are also oxidized in acid solution giving phosphorous acid:[36-38]

$$IO_3^- + 3H_3PO_2 \rightarrow I^- + 3H_3PO_3.$$

There is an induction period to this reaction[37] and the study of its rate is further complicated by the ensuing reaction between the iodide ions produced and more iodate. This difficulty can be minimized by adding silver chloride, which reduces the iodide concentration, and also by adding propanol, which inhibits the iodate-iodide reaction. Under these conditions, the rate of oxidation of hypophosphorous acid is given by:

$$-d[IO_3^-]/dt = \frac{k_1[H^+][H_3PO_2]}{1 + k_2[H^+]/k_3[IO_3^-]}$$

where the values of the constants at 30°C. are: $k_1 = 9{\cdot}7$ moles^{-1}litre hour^{-1} and $k_2/k_3 = 0{\cdot}44$.[38] In neutral or alkaline solution there is no reaction between iodates and hypophosphites.[39] With excess of iodic acid, phosphorous acid is further oxidized to phosphoric acid.[36] The reaction is slow at room temperatures and there is a considerable induction period which is increased by adding propanol.[40] In aqueous sulphuric acid solution elementary phosphorus is oxidized by iodates to phosphoric acid. To complete the oxidation the sulphuric acid must be at least 0·25 N. and the solution should be refluxed for 3 hours.[41]

Thiocyanates are quantitatively oxidized by acid iodate solutions. In hydrochloric acid solution, the reaction is

$$2SCN^- + 3IO_3^- + 2H^+ + Cl^- \rightarrow 2SO_2^{--} + 2ICN + ICl + H_2O.$$

In determining thiocyanates by titration with iodate, the acid concentration should be not less than 1 N. and the thiocyanate concentration not less than 0·0001 N.[42]

Arsenious acid is oxidized by iodic acid to arsenic acid. The rate of reaction was found to be independent of the arsenious acid concentration and it was suggested that the rate-determining step in this reaction is the production of hypoiodite ions by a small, catalytic quantity of iodide ions:

$$IO_3^- + 2I^- + H^+ \rightarrow HIO + 2IO^-.$$

The hypoiodite ion is considered to be the effective oxidizing entity.[43] Oxalic acid is oxidized by iodic acid according to the equation:

$$5(COOH)_2 + 2HIO_3 = 10CO_2 + I_2 + 6H_2O.$$

The kinetics of this reaction have also been investigated.[44] Selenium dichloride is oxidized by iodic acid to selenium dioxide.[45]

Quinquevalent molybdenum is oxidized quantitatively by iodic acid. In 4N-hydrochloric acid solution, this reaction is a convenient way of determining molybdenum.[46] In hot alkaline solution, iodates oxidize vanadyl salts to the hexavalent state:[47]

$$6VOSO_4 + KIO_3 + 18KOH \rightarrow 6KVO_3 + 6K_2SO_4 + KI + 9H_2O.$$

Under the same conditions, iodates are themselves oxidized to periodates by potassium permanganate.[48] Iodates are reduced by magnesium amalgam to the corresponding iodides.[49]

Iodates are detectable by virtue of their oxidizing properties. Leucofluorescein reagent, prepared by dissolving 20 mg. of fluorescein in 10 ml. of 5% caustic soda solution and decolourizing it with 2 ml. of 5% sodium amalgam, is stable for 24 hours but its colour is immediately restored by iodate ions. Iodate concentrations of 1 part in 700,000 are detectable in this way.[50] The analytical applications of iodic acid and its salts have been recently reviewed.[51]

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THE PREPARATION AND PROPERTIES OF THE METAL IODATES

Alkali metal iodides can be oxidized directly to iodates by oxygen at pressures of 100 atmospheres and above.[1a-1c] The oxidation can be carried out in aqueous solution at temperatures up to 500°C. and in the molten state up to 630°C.[1b] The reaction in both cases is facilitated by the presence of alkali hydroxides and also of catalytic oxides such as those of bismuth and aluminium.[1a,1c]

Lithium iodate crystallizes with a hexagonal close-packed structure. The unit cell contains 2 molecules and has the dimensions $a = 5{\cdot}469 \pm 0{\cdot}003$ A. and $c = 5{\cdot}155 \pm 0{\cdot}005$ A. The Li – O and O – I distances are both 2·23 A.[2a] The density of lithium iodate at 32°C. is 4·502 g.per c.c.[2b] Lithium iodate is very soluble in water and the electrical conductivity[3] and viscosity[4] of aqueous solutions have been studied. The molar magnetic susceptibility, χ_m, of lithium iodate in aqueous solution was found[5] to be $-46{\cdot}7 \times 10^{-6}$ c.g.s. units. The Faraday effect of aqueous lithium iodate solution was determined at 0°C. using light of wavelength 5460 A. and the relative molecular magnetic rotation was found to be 10·22, the contribution of the iodate ion being 10·12.[6,7] Lithium iodate is only slightly soluble in acetone.[8]

Sodium and potassium iodates may be prepared by oxidation of the corresponding iodide.[9] Anhydrous sodium iodate crystallizes from water, forming orthorhombic crystals with the space group V_h^{16}– $Pbnm$. There are 4 molecules in the unit cell which has the dimensions $a = 5{\cdot}75$ A., $b = 6{\cdot}37$ A., and $c = 8{\cdot}10$ A.[10-12] The structure contains distinct pyramidal IO_3 groups[10-12] in which the I – O distance is 2·06 A.; the Na – I distance is 3·48 A.[10] The density of sodium iodate at 32°C. is 3·621 g.per c.c.[2b] The compressibility of sodium iodate, potassium iodate and ammonium iodate for pressures up to 25,000 kg.cm.$^{-2}$ has been measured[13] and the relative change in volume with applied pressure is shown in Table VI.

TABLE VI. - COMPRESSIBILITY OF SODIUM, POTASSIUM AND AMMONIUM IODATES

Pressure kg. cm.$^{-2}$	$\Delta V/V_0$ $NaIO_3$	$\Delta V/V_0$ KIO_3	$\Delta V/V_0$ NH_4IO_3
2,000	0·0068	0·0068	0·0057
5,000	0·0165	0·0161	0·0138
10,000	0·0312	0·0298	0·0266
15,000	0·0444	0·0417	0·0384
20,000	0·0546	0·0522	0·0490
25,000	0·0675	0·0619	0·0586

The standard entropy of crystalline sodium iodate, $S^\circ_{298\cdot1}$°K., has been calculated to be 32·3 ± 1·0 g.-cal.mole^{-1}deg.$^{-1}$ [14]

The earlier measurements of the solubility of sodium iodate in water have been confirmed and extended[15-17] and some recent results are shown in Table VII.

TABLE VII. - SOLUBILITY OF SODIUM IODATE IN WATER

t°C.	0	5	10	15	19·85	25	30	35
Solubility %W/W	2·42	3·30	4·39	5·86	7·83	8·67	9·63	10·58
t°C.	40	50	60	70	80	90	100	
Solubility %W/W	11·71	14·0	16·5	19·0	21·0	22·8	24·8	

Only two hydrates of sodium iodate have been confirmed. Up to 19·85°C. the saturated solution is in equilibrium with the pentahydrate, $NaIO_3,5H_2O$; from 19·85 to 73·4°C. $NaIO_3,H_2O$ is the stable hydrate, and above this temperature anhydrous sodium iodate crystallizes from solution.[15-17] The solubility, S, in wt. per cent., of the monohydrate from 20°C. to 50°C. can be represented[15] by the equation:

$$\log S = 3{\cdot}6344 - \frac{802{\cdot}8}{T}$$

and that of the pentahydrate from 0°C. to 15°C. by

$$\log S = 7{\cdot}7793 - \frac{2{\cdot}019}{T}\,.$$

The freezing point of a saturated aqueous solution of sodium iodate is[15,18] −0·35°C. The differential and integral heats of dilution of aqueous sodium iodate solutions at concentrations less than 0·1 N. have been determined calorimetrically at 25°C. and are in agreement with the values predicted from the corresponding activity coefficients.[19] Volume contractions on dissolving 1 mole of $NaIO_3$ in water were found to be 20·86, 15·54 and 3·50 c.c. for 1,5 and 10% w/v solutions respectively.[20] The compressibility of sodium iodate and potassium iodate solutions has been calculated from the velocity of ultrasonic sound in these solutions.[21] The equivalent conductances of sodium and potassium iodates in dilute solution at 18°C. have been measured accurately[22] and some results are shown in Table VIII.

TABLE VIII.- EQUIVALENT CONDUCTANCE OF DILUTE AQUEOUS SOLUTIONS OF SODIUM AND POTASSIUM IODATES

Concentration mole litre^{-1} × 10^4	5	10	50	100	200
$NaIO_3$	75·81	75·17	74·61	70·84	68·56
KIO_3	96·70	96·02	93·18	91·22	88·62

These data are in complete agreement with the extended Onsager–Shedlovsky equation and lead to limiting equivalent conductance values, Λ_0, for sodium and potassium iodate of 77·32 and 98·33 $ohm^{-1}cm.^2mole^{-1}$ respectively.[22] Sodium iodate is insoluble in ethylenediamine.[23]

The solubility of sodium iodate in various aqueous salt solutions has been determined as part of the investigation of ternary systems including sodium iodate and water. In the system, $NaIO_3$–NaI–H_2O, three double salts are found,[24,25]

$2NaIO_3,3NaI,20H_2O$,
$2NaIO_3,3NaI,15H_2O$,
$2NaIO_3,3NaI,10H_2O$,

In the system, $NaIO_3$–$NaBr$–H_2O, the double salts

$2NaIO_3,3NaBr,15H_2O$,
$2NaIO_3$,[illegible]$NaBr,10H_2O$

were isolated, the former existing from 5° to 40°C. and the latter from 40° to 50°C.[26] The double salts

$2NaIO_3,3NaCl,3H_2O$, [27]
$2NaIO_3,3NaNO_3,15H_2O$, [16,17]
$NaIO_3,3Na_2SO_4$, and
$NaIO_3,4Na_2SO_4$ [28]

have also been detected. No compound formation has been observed in the corresponding ternary systems:

$NaIO_3$-$NaClO_3$-H_2O, [29]
$NaIO_3$-KIO_3-H_2O, [30]
$NaIO_3$-$Mg(IO_3)_2$-H_2O, [30]
$NaIO_3$-$Ca(IO_3)_2$-H_2O, [31]
$NaIO_3$-Na_2CO_3-H_2O, [32]
$NaIO_3$-$Na_2C_2O_4$-H_2O, [33]
$NaIO_3$-Na_2MoO_4-H_2O. [34]

Below 37°C. sodium iodate monohydrate and potassium chloride can co-exist in solution but above this temperature only sodium chloride and potassium iodate can exist in equilibrium with each other and the saturated solution.[35]

Potassium iodate is rapidly formed when potassium iodide is fused with potassium chlorate, bromate or perchlorate. In each case there is a large evolution of oxygen and yields varying from 40 to 80% are obtained.[36a] The purification of potassium iodate and its use as an analytical standard have been described in detail.[36b] Where sodium iodate is present as impurity, recrystallization of the potassium salt from water increases its sodium content.[36c] Potassium pyroiodate, KI_3O_8, has been prepared by heating the normal iodate with iodine pentoxide in a sealed tube at 170°C. for 60 hours. Its structure was examined by the *X*-ray powder technique and its melting point was found to be 316°C.[37]

Normal potassium iodate, KIO_3, crystallizes in the monoclinic system with a caesium chloride type structure, the unit cell dimensions being 4·57, 4·50 and 4·50 A.[38a,38b] Single crystals have been shown to be piezo-electric.[39a] The compressibility of solid potassium iodate is recorded in Table VI. Its density has been measured at 32°C.[2b] and at temperatures from 15°C. to −273°C.,[39b] some results being shown in Table IX.

TABLE IX. - DENSITY OF POTASSIUM IODATE

Temperature, °C.	32	15	−78	−194	−273
Density, g. c. c.$^{-1}$	3·93	3·990	4·025	4·068	4·085

Its molar volume at absolute zero was calculated to be 52·4 c.c.[39] The cooling curve of potassium iodate shows a definite plateau at 150°C. which suggests an allotropic modification.[40]

The molal heat capacity of potassium iodate has been determined for the temperature range 17·30°K. to 298·1°K. and its entropy has been calculated to be 36·20 g.-cal.deg.$^{-1}$mole^{-1}.[41] Some of the data on which this figure is based are given in Table X.

TABLE X. - MOLAL HEAT CAPACITY OF POTASSIUM IODATE

Temperature, °K.	17·30	20·2	23·38	31·35	41·02	51·87
Molal heat capacity, g.-cal.mole^{-1}deg.$^{-1}$	1·245	1·795	2·451	4·488	6·789	9·134
Temperature, °K.	64·36	81·96	105·93	156·05	201·79	295·00
Molal heat capacity, g.-cal.mole^{-1}deg.$^{-1}$	11·30	13·73	16·25	19·88	22·29	25·24

The dielectric constant of solid potassium iodate was found to be 16·85.[42]

Further determinations of the solubility of potassium iodate in water have been carried out.[43] The most recent values are shown in Table XI. Solubility determinations have also been extended to temperatures up to 450°C.[44] Potassium iodate is less soluble in heavy water, D_2O, the ratio of the solubilities in light and heavy water at 25°C. being 0·833.[45] The volume contraction on dissolving 1 mole of potassium iodate in an infinite volume of water at 25°C. has been estimated to be 2·4 c.c.[46]

TABLE XI. - SOLUBILITY OF POTASSIUM IODATE IN WATER

Temperature, °C.	15	20	25
Solubility, %W/W.	6·684	7·478	8·343
Molality of the saturated solution.	0·331	0·372	0·417
Specific gravity of the saturated solution.	1·0584	1·0643	1·0708

The activity coefficients of potassium iodate in aqueous solution have been studied cryoscopically[47] and the effect of ion-association in these solutions has been discussed.[48] The conductance of aqueous potassium iodate solutions at 25°C. has been measured over the concentration range 0·001 to 0·1 molal.[49-51] The most recent value for the limiting equivalent conductance is 114·27 $\text{ohm}^{-1}\text{cm.}^2\text{mole}^{-1}$, which leads to an ionic conductance of 40·75 for the iodate ion and to a value of 1·7 for the ion-pair dissociation constant.[51] The dielectric constant of aqueous potassium iodate solutions has been shown to increase linearly with concentration[52,53] and from these data the molar polarization of potassium iodate was calculated to be 302·9c.c.[52] Its molar susceptibility in aqueous solution is -46.7×10^{-6} c.g.s. units.[5] The diffusion of potassium iodate at a boundary separating its solution and a solution of potassium chloride has been studied using the schlieren scanning-camera technique.[54] The diffusion of potassium iodate through a semi-permeable membrane of copper ferrocyanide has been investigated[55] as also has its adsorption on Cellophane[56] and pectin.[57]

The solubility of potassium iodate in other potassium salt solutions has been measured. No evidence of double salt formation was observed in the ternary systems of potassium iodate and water with potassium iodide,[58] potassium bromide,[26] potassium chloride,[30] potassium chlorate,[29] potassium nitrate[31] or potassium sulphate.[30] No hydrate of potassium iodate has been isolated. The solubility of potassium iodate in dioxan-water mixtures has been measured as part of an investigation of the hypothesis that the activity coefficient of a salt in any saturated solution is independent of the dielectric constant of the medium; good agreement with this theory was observed.[59] Potassium iodate is only slightly soluble in liquid ammonia,[60] and at 25°C. the molality of a saturated solution (under pressure) is[61] $3{\cdot}044 \times 10^{-5}$. By measuring the increase in its solubility in ammonia that occurs on the addition of various soluble salts, a relation for the variation of activity coefficient with ionic strength was obtained and the mean activity coefficient in the saturated solution was calculated to be 0·891.[61] Potassium iodate is also slightly soluble in liquid sulphur dioxide,[62,63] appreciably soluble in liquid phosphorus oxychloride[64] but quite insoluble in ethylenediamine and monoethanolamine.[23]

Aqueous potassium iodate solutions are reduced by irradiation with *X*-rays[65,66] and with α-particles,[66] the iodide being formed in each case. Solid potassium iodate is also reduced by hydrogen and by carbon monoxide.[67]

Rubidium pyroiodate was prepared by heating the normal iodate with iodine pentoxide in a sealed tube at 170°C. for 60 hours. Its structure was investigated by the *X*-ray powder technique. It was found to melt at 340°C. with decomposition.[37] *X*-Ray investigation has shown that normal rubidium iodate, $RbIO_3$, has a perovskite structure with the a distance equal to 4·52 ± 0·02 A.[37] Its density at 32°C. is 4·471 g. per c.c.[2b]

Ammonium iodate has an orthorhombic structure similar to that of sodium iodate[12] and not the perovskite structure suggested earlier.[68] Interpretation of the results of the *X*-ray studies is complicated by twinning, but the cell dimensions have been established as $a = 6{\cdot}41$, $b = 6{\cdot}38$ and $c = 9{\cdot}25$ A.[12] The density of ammonium iodate is 3·42 g. per c.c.[2b] and its volume contraction under high pressures is tabulated above. Its molar magnetic susceptibility in aqueous solution is $-62{\cdot}3 \times 10^{-6}$ c.g.s. units.[5]

Silver iodate, prepared by double decomposition of an alkali iodate and silver nitrate in aqueous solution, can be crystallized and purified by slow evaporation of an ammoniacal solution.[69,70] It can also be prepared by shaking a suspension of silver bromate in water with potassium iodate.[71] The preparation of silver iodate, its microcrystalline structure and its solubility in water have been discussed.[70] The unit cell has a = 7·24 A., b = 5·77 A., c = 15·13 A Comparison of observed and calculated densities indicates 7·66 molecules per unit cell, and subperiodicity in the lattice or a faulty structure is postulated. The space-group is $D_{2h}^{15}[-Pbca]$.[126] Solid silver iodate can be heated to 410°C. without decomposition.[72] Its solubility in water at 75°C. has been determined and was found to be 0·000840 molal.[73] The dependence of the solubility on ionic strength, varied by the addition of several electrolytes, is in accord with the Debye-Hückel theory.[73] Saturated solutions of silver iodate often contain a smaller concentration of silver ions than of iodate ions owing to exchange reactions with the glass container.[74] The solubility of silver iodate and its mean activity coefficients in nitric acid and potassium nitrate solutions have been measured using a silver-silver iodate electrode.[74,75] The standard potential of this electrode and the thermodynamic solubility product of silver iodate over the temperature range 10° to 35°C. were found to have the values given in Table XII.[75]

TABLE XII. - STANDARD ELECTRODE POTENTIAL AND THERMODYNAMIC SOLUBILITY PRODUCT OF SILVER IODATE

Temperature, °C.	10	20	25	30	35
E_0, V.	0·3625	0·3576	0·3550	0·3524	0·3498
$K_s \times 10^8$	0·923	2·078	3·055	4·490	6·456

The corresponding thermodynamic quantities, $\Delta G°$, $\Delta S°$, $\Delta H°$ and $\Delta C_p°$, for the reaction $AgIO_3 \rightarrow Ag^+ + IO_3^-$ were also derived[75] and are given in Table XIII.

TABLE XIII. - THERMODYNAMIC DATA FOR THE REACTION $AgIO_3 \rightarrow Ag^+ + IO_3^-$

Temperature	Values in g.-cal.mole.$^{-1}$			
	$\Delta G°$	$\Delta S°$	$\Delta H°$	$\Delta C_p°$
10	10,415	10·96	13,515	1·31
20	10,300	11·00	13,528	1·35
25	10,252	11·03	13,535	1·38
30	10,190	11·05	13,542	1·40
35	10,142	11·07	13,549	1·42

The stability of the monammine-silver ion, $AgNH_3^+$, has been studied by measuring the solubility of silver iodate in dilute ammonia solutions, some values for which are shown in Table XIV. From these data, the instability constant of the monammine-silver ion was calculated as $4{\cdot}3 \times 10^{-4}$ and that of the diammine-silver ion, $Ag(NH_3)_2^+$, as $6{\cdot}2 \times 10^{-8}$.[76] The solubility of silver iodate in aqueous solutions of pyridine,[77] glycine, alanine,[78] and gelatin[79] and in aqueous solutions of other metal ammoniates[80,81] has also been deter-

TABLE XIV.- SOLUBILITY OF SILVER IODATE IN AQUEOUS AMMONIA

Concentration of ammonia, molality × 10^2	1·26	1·94	8·42	41·0	82·3
Solubility of silver iodate, molality × 10^4	2·25	2·39	3·43	13·02	25·90

mined. The rhythmic precipitation of silver iodate on gelatin has been described.[82] The adsorption of radioactive elements on silver iodate has been measured and discussed in terms of the Verwey–Kruyt theory,[83a] a ψ_0 value of −31mV. being obtained.[83b] Silver iodate reacts with tellurium tetrabromide to form the di-iodate, $Te(IO_3)_2$.[84]

Blue cupric iodate monohydrate and white anhydrous cupric iodate have been described. From ammoniacal solution, the penta-, the tetra- and the di-ammoniates have been crystallized and characterized. The density of the monohydrate was found to be 4·83 and that of the penta-ammoniate 2·811.[85] The solubility of cupric iodate in aqueous solutions of glycine, alanine and gelatin has been measured and the equilibrium constants for the interaction of the copper ion with the amino acids have been determined.[86]

The alkaline earth iodates can be prepared by passing chlorine into a boiling solution of the corresponding hydroxide in which iodine has been dissolved. There is no periodate formation.[87] Calcium iodate, $Ca(IO_3)_2$, occurs naturally as the mineral lautarite. Its crystal structure is cubic and is similar to that of potassium iodate.[88] There are 4 molecules per unit cell, the constants of which are a = 7·18 A., b = 11·38 A., c = 7·42 A. and β = 106°22′.[89] The two modifications of calcium iodate hexahydrate reported earlier (Mellor, II, 347) have since been shown to be identical. The structure is orthorhombic and the ratios of the cell constants $a : b : c$ are 0·6465 : 1 : 0·2768.[90] Anhydrous calcium iodate is stable up to 540°C.[91] Its molar magnetic susceptibility is −101·4 × 10^{-6} c.g.s. units.[5] The hexahydrate is decomposed by a silent electric discharge to calcium iodide.[92]

The solubility of calcium iodate in water at 25°C. is 3·301 g. of $Ca(IO_3)_2$ per 1000 g. of water,[93-95] the solid phase in equilibrium with the solution being the hexahydrate. Its solubility in several salt solutions, particularly those of other iodates, has also been determined.[93-99] These results together with those from electrical conductance studies[94] indicate that calcium iodate is not completely dissociated in aqueous solution. From the variation of equivalent conductivity with concentration of calcium iodate, the dissociation constant of the ion-pair, $CaIO_3^+$, is calculated to be 0·13 g.-ion litre^{-1} at 18°C.[94] The solubility and dissociation of calcium iodate in calcium and sodium lactate solutions,[100] in dilute ammonia solutions,[101,102] and in glycine, alanine[103] and other amino-acid solutions[104] have been studied. A complex calcium aluminium iodate has been prepared by mixing an aqueous calcium iodate solution with sodium aluminate solution. It has the formula $5CaO,Al_2O_3,Ca(IO_3)_2,34H_2O$ and separates in small needle-like crystals, an X-ray study of which suggests that it has the cell dimensions a = 11·15 A. and c = 20·9 A.[105]

Anhydrous strontium iodate[106] and strontium iodate hexahydrate[107] have been characterized. The isothermal dehydration of the hexahydrate under reduced pressure has been observed with an electron microscope and it was seen that the essential macro-crystalline structure is retained even when all the water has been removed.[107] Anhydrous strontium iodate has been shown to be stable up to 750°C.[106] Its molar magnetic susceptibility is −108 × 10^{-6} c.g.s. units.[5]

Barium iodate is stable up to 720°C.[106] and has a molar magnetic susceptibility of −122·5 × 10^{-6} c.g.s. units.[5] Its solubility in water[99,109] and in numerous salt solutions has been measured;[108-110] in water at 25°C. it is 0·812 millimole litre^{-1}.[99] Barium iodate is also incompletely dissociated in aqueous solution and the dissociation constant of the ion-pair, $BaIO_3^+$, is reported to be 0·08 g.-ion litre^{-1}.[109] The solubility of barium iodate in water–dioxan mixtures containing from 0 to 100% dioxan has been determined. The variation in solubility with changing dielectric constant was found not to be in accord with the Born equation.[111] The solubility of barium iodate in ammonia,[36] and in glycine and alanine[103] solutions has been measured. The distribution of radium ions between barium iodate crystals and a saturated aqueous solution of barium iodate has been investigated[112] and is in good agreement with that predicted by Ratner's theory.[113] The solubility of radium iodate itself in water varies almost linearly from 0·305 millimole litre^{-1} at 0°C. to 2·96 millimoles litre^{-1} at 100°C. The variation in solubility with the concentration of several added electrolytes has been investigated.[114]

The solubility of magnesium iodate in water from the eutectic point, -0·36°C., to +90°C. has been determined,[115] and some of these results are shown in Table XV together with the corresponding density of the saturated solution.

TABLE XV. - SOLUBILITY OF MAGNESIUM IODATE IN WATER

Temperature °C.	Solubility %W/W $Mg(IO_3)_2$	Density of saturated solution, g. c.c.$^{-1}$.
-0·36	3·18	1·026
+5	4·39	1·034
10	5·87	1·049
15	7·29	1·065
25	8·55	1·075
35	9·83	1·086
50	12·05	1·115
70	13·3	–
90	13·5	–

The saturated solution is in equilibrium with the decahydrate, $Mg(IO_3)_2,10H_2O$, below 13·3°C. and with the anhydrous salt above 57·5°C. The normal tetrahydrate is very stable and may be dried over phosphorus pentoxide without loss of water.[115] No double salts were found in the ternary system $Mg(IO_3)_2$–$NaIO_3$–H_2O.[30]

The densities of several zinc iodates have been determined. The dihydrate, $Zn(IO_3)_2,2H_2O$, was crystallized from a mixture of zinc nitrate solution and iodic acid solution; its density at 25°C. is 4·223. Anhydrous zinc iodate is obtained by heating the dihydrate to 100°C. for an hour; its density is 5·063.[116] Its solubility in various water–dioxan mixtures has been investigated.[59] A new ammoniate, $Zn(IO_3)_2,2NH_3$, has been prepared by heating the tetra-ammoniate at 128°C. for 8 hours. It has a density at 25°C. of 3·583.[116] The solubility of cadmium iodate in various salt solutions has been investigated.[117,118] The preparation of mercurous iodate by adding iodic acid or sodium iodate to mercurous nitrate solution has been confirmed. A pure white product which is neither soluble in excess of iodate nor decomposed by boiling water is obtained in this way.[119] At 14°C. its solubility in water is approx. 0·06 g. litre^{-1}.[120] Mercurous iodate is decomposed by ammonia solution forming eventually amido-mercuric iodate, $H_2N{\cdot}Hg{\cdot}IO_3$.[119] Mercuric iodate can also be prepared by simple double decomposition. It is soluble in mineral acids and also in alkali halide solutions and should, therefore, not be prepared from halide-containing salts. Its micro-crystalline structure and its use in analytical chemistry have been discussed.[121]

Aluminium iodate is very soluble in water and is crystallized only with difficulty. Equimolecular quantities of aluminium nitrate and iodic acid are mixed in aqueous solution and the mixture is then evaporated in vacuo over sulphuric acid until a syrup is obtained. On standing, this syrup yields crystals of the hexahydrate $Al(IO_3)_3,6H_2O$. In the presence of excess of iodic acid, aluminium iodate-nitrate, $Al(IO_3)_2NO_3,6H_2O$, has been obtained. It is suggested that the structure of both is that of a hexaquo complex cation.[122]

Gallium iodate has been prepared by dissolving gallium metal in nitric acid and adding excess of iodic acid; the anhydrous salt, $Ga(IO_3)_3$, precipitates. From neutral solution, using sodium iodate, a basic iodate, $Ga(IO_3)_3,2Ga(OH)_3$, is obtained.[123] Indium iodate, $In(IO_3)_3$, on the other hand can be prepared in neutral or acid solution. From a mixture of indium sulphate and potassium iodate in aqueous solution, the white amorphous salt is precipitated and can be filtered, washed and dried in the usual way. It is sparingly soluble in water, 1 litre of water at 20°C. dissolving 0·53 g. It is more soluble in nitric acid, (1 litre of 30% aqueous HNO_3 dissolving 16·89 g.) and may be recrystallized from this solution to give small white crystals.[124]

Thallous iodate has been shown to have a slightly distorted perovskite structure and to show rhombohedral symmetry;[125] $a = 4{\cdot}44$ A., $\alpha = 89°6'$. Its standard entropy at 25°C. has been calculated as $42{\cdot}9 \pm 1{\cdot}5$ g.-cal.deg.$^{-1}$mole^{-1}.[14] Its solubility in water at 25°C. is 0·001844 mole litre^{-1}.[127] The solubility of thallous iodate in various salt solutions has been the subject of many electrochemical investigations which have shown that, if ion-association is taken into account, a mean activity coefficient of thallous iodate in agreement with the Debye–Hückel theory is obtained.[128-130] The solubility of thallous iodate in amino-acid solutions,[131,132] in carboxylic acid solutions[134] and in ethyl alcohol–water mixtures[134] has also been investigated.

Similar electrochemical studies have been made of lanthanum iodate[127-129,135] and cerous iodate.[136] The solubility of lanthanum iodate in water at 25°C. is $8{\cdot}9 \times 10^{-4}$ mole litre^{-1},[127] and that of cerous iodate 1·732 g. per 1000 g. of water.[136] Gadolinium iodate is precipitated immediately when solutions of gadolinium chloride and sodium iodate are mixed. The granular precipitate can be dried in air and has the formula $Gd(IO_3)_3,5\frac{1}{2}H_2O$.[137] Europium iodate has been prepared in a similar way from europium acetate and iodic acid. It also crystallizes with 5½ molecules of water, having the empirical formula $Eu(IO_3)_3,5\frac{1}{2}H_2O$.[138]

Plumbous iodate, $Pb(IO_3)_2$, is precipitated from a solution of any soluble lead salt to which an iodate is added. It is not stable in the presence of hydrochloric or sulphuric acid. It is stable and insoluble in the presence of excess of iodate ions and use may be made of this fact in the determination of lead.[139] Lead iodate can be safely heated up to 400°C.[140] The most recent value[141] for the solubility of plumbous iodate in water is $3{\cdot}61 \times 10^{-5}$ mole litre^{-1} at 25°C., a value considerably lower than those reported earlier (Mellor, II,356) and probably based on a purer product.[142] The solubility of plumbous iodate in solutions of glycine and alanine[78] and in various salt solutions[142,143] has also been studied and has been shown to increase rapidly with the concentration of anions such as chloride, acetate etc., which form complex ions with the lead.[142,143] The rhythmic precipitation of lead iodate in gelatin has been described.[144,145] The specific magnetic susceptibility of plumbous iodate was found to be $-0{\cdot}2356 \times 10^{-6}$ c.g.s. units, from which the ionic susceptibility of the bivalent lead ion is calculated to be -38×10^{-6} c.g.s. units.[146] Several iodates of tetravalent lead have also been described. When a solution of lead tetra-acetate in glacial acetic acid is added slowly to an equimolecular quantity of iodic acid in 50% acetic acid, a yellow precipitate of the dihydrate, $Pb(IO_3)_4,2H_2O$, is obtained. By drying this compound at 120°C., anhydrous plumbic iodate, $Pb(IO_3)_4$, is formed. If three times this quantity of iodic acid is used, an acid iodate, $Pb(IO_3)_4,2HIO_3,2H_2O$, is formed. It is suggested that this compound is a complex acid of the hexaiodatoplumbic anion, $H_2Pb(IO_3)_6,2H_2O$, and the lithium, sodium, potassium and ammonium salts of this acid were obtained simply by employing the corresponding metal acetate in the preparation. In each case, the dihydrate was obtained, $M_2Pb(IO_3)_6,2H_2O$.[147] Both tin[148] and titanium[2b] form complex hexaiodates in exactly the same way. Titanium can be estimated as potassium titani-iodate and this can be safely dried at temperatures up to 295°C.[149] Thorium is often determined simply as the iodate, $Th(IO_3)_4$, which is precipitated from neutral or acid solution. Thorium iodate can be safely dried at temperatures up to 300°C.,[150] and various procedures have been suggested for the recovery of the iodate from this determination.[151] Thorium iodate does not react with liquid ammonia; its solubility therein at 25°C. is 0·8 g. per 1000 g. NH_3.[152]

Three hydrated chromium iodates have been described. From aqueous solutions of chromium nitrate and an alkali iodate, a green voluminous precipitate of the pentahydrate, $Cr(IO_3)_3,5H_2O$, is obtained. On drying at 100°C. this loses three molecules of water, forming the dihydrate, $Cr(IO_3)_3,2H_2O$. An intermediate hydrate of the formula $Cr(IO_3)_3,4\frac{1}{2}H_2O$ is formed when the pentahydrate is suspended in acid solution and heated to 100°C. for some time.[122] Several double iodates of trivalent manganese have been described. All are of the type $M_2Mn(IO_3)_5$, where M is any alkali metal or ammonium ion.[153]

Brownish-yellow ferric iodate, $Fe(IO_3)_3$, is precipitated when an acid solution of ferric nitrate or ferric ammonium sulphate is added to iodic acid solution. The anhydrous salt is obtained by filtration and drying; there is no evidence of hydrate formation. If the precipitation is carried out in neutral solution, some co-precipitation with alkali iodate takes place.[122]

The preparation of anhydrous cobaltous iodate, $Co(IO_3)_2$, and of the di- and tetra-hydrates of this salt has been re-investigated. The densities of these compounds at 25°C. were found to be 4·931, 4·160 and 3·46 respectively. Two new ammoniates, $Co(IO_3)_2,6NH_3$ and $Co(IO_3)_2,2NH_3$, have been isolated.[116] The solubility of cobaltous iodate[154] and several cobaltammine iodates[155] in various salt solutions has been determined. The existence of yellow anhydrous nickel iodate, $Ni(IO_3)_2$, and of the green dihydrate, $Ni(IO_3)_2,2H_2O$, has been confirmed, although it is claimed that the anhydrous salt obtained by direct crystallization is different from that obtained by dehydrating the dihydrate. The density of the anhydrous salt was found to be 5·02, that of the dihydrate 4·01 and that of the hexammoniate, $Ni(IO_3)_2,6NH_3$, 2·557.[85]

Three uranium iodates have been prepared by adding uranic sulphate solution to iodate solutions of varying degrees of acidity. In slightly acid solution, uranyl iodate, $UO(IO_3)_2$, is formed but in more strongly acid solution the normal iodate $U(IO_3)_4$ is precipitated. With a large excess of iodic acid present, an acid iodate, $U(IO_3)_4,2HIO_3$, can be crystallized from the solution.[156] Several plutonium iodates have also been studied. The tri- and tetra-iodates, $Pu(IO_3)_3$ and $Pu(IO_4)_4$, have been isolated and their solubilities in water determined approximately.[157,158]

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THE PREPARATION OF PERIODIC ACID AND PERIODATES

Periodic acid and most metal periodates are prepared from an alkali metal periodate, which is usually obtained by oxidation of the corresponding iodate with a powerful oxidizing agent such as chlorine, bromine or potassium permanganate. The optimum experimental conditions for the preparation of sodium paraperiodate, metaperiodate and orthoperiodate have been recorded.

Trisodium paraperiodate, $Na_3H_2IO_6$, can be prepared by dissolving 233 g. of sodium iodate and 140 g. of sodium hydroxide in 600 ml. of water at 50°C. and bubbling chlorine rapidly through the solution. After oxidation is complete, the solution is made slightly alkaline with more sodium hydroxide to convert any disodium paraperiodate, $Na_2H_3IO_6$, into the less soluble trisodium salt, $Na_3H_2IO_6$, which separates in 97 – 98% yield when the solution is cooled. Alternatively, 233 g. of sodium iodate and 40 g. of sodium hydroxide are dissolved in 1200 ml. of water. This solution is heated to boiling and, with vigorous mechanical stirring, first 213 g. of potassium persulphate and then 170 g. of sodium hydroxide are added slowly in small portions. The solution is boiled for a further 15 minutes, cooled to 40°C. and the trisodium paraperiodate filtered off and washed free from sulphate.[1] If the solution is cooled below 40°C., large amounts of sulphates also crystallize. Sodium paraperiodate may also be prepared directly from iodine. Sodium hydroxide (264 g.) and iodine (50 g.) are dissolved in 2 litres of water contained in a 4-litre beaker. The solution is heated to 80°C. and, with constant stirring, 80 ml. of bromine are slowly added at a rate sufficient to maintain the solution at 80°C. On cooling the solution, the trisodium paraperiodate separates in yields varying from 93 to 98%.[2,3] Potassium paraperiodate can be prepared in the same way.[1]

Sodium metaperiodate, $NaIO_4$, is obtained by acidifying solutions of sodium paraperiodate: to 100 g. of sodium paraperiodate dissolved in 200 ml. of water 55 g. of concentrated nitric acid is added and the solution, filtered if necessary, is evaporated on a steam bath until crystals appear. The solution is then cooled to 20°C. and filtered; the precipitate is washed with cold water and dried at 110°C. If the solution is over-cooled, crystals of the trihydrate, $NaIO_4,3H_2O$, may form. Potassium metaperiodate can be prepared in the same way.[1]

Pentasodium paraperiodate, Na_5IO_6, (often referred to as the ortho periodate) can be prepared by the reaction of gaseous oxygen with mixtures of of sodium iodide and sodium oxide, hydroxide or peroxide at elevated temperatures. Oxygen uptake begins at 200°C., and at 300 – 400°C. the reaction, $NaI + 2Na_2O + 2O_2 \rightarrow Na_5IO_6$, is complete within a few minutes, although temperatures as high as 700°C. are often employed. The product is approximately 99% pure. Recrystallization from water yields the paraperiodate, $Na_3H_2IO_6$. Sodium nitrate catalyzes the oxidation and does not interfere with the yield.[4] Periodates are also formed by anodic oxidation of alkali metal iodate solutions using a platinum or lead dioxide electrode,[5] and by the action of potassium permanganate on acid iodate solutions.[6]

The acidification of alkali metal periodate solutions and their subsequent evaporation yields only the corresponding metaperiodate; hence to obtain pure periodic acid it is necessary to prepare first either silver or barium paraperiodate and then remove the metallic component. The exact experimental details of both processes have been recorded. Sodium paraperiodate solution is neutralized with nitric acid and secondary silver mesoperiodate, Ag_2HIO_5, is precipitated by adding an exactly equivalent amount of silver nitrate. The precipitated silver salt is filtered off, washed, suspended in water and, at 70°C., is treated with an excess of bromine, which is added gradually with stirring. The solution is separated from the precipitated silver bromide and freed from excess of bromine by a brisk current of air. It is then evaporated under reduced pressure using both sulphuric acid and solid sodium hydroxide as desiccants. On cooling the concentrated solution, clear, brilliant crystals of paraperiodic acid, H_5IO_6, are formed; periodic acid solutions tend to supersaturate rather readily and sufficient time should be allowed for the crystallization to become complete. The crystals can be separated from the mother liquor by using a centrifuge, and are dried at 50°C. in vacuo. A 93% yield of paraperiodic acid can be obtained in this way.[3]

In the alternative method, barium nitrate solution is added to slightly acid sodium paraperiodate solution. The solution is boiled for 2 hours, neutralized with barium hydroxide solution and allowed to cool. Barium paraperiodate, $Ba_3H_4(IO_6)_2$, crystallizes from the solution and is filtered off and washed well with cold water. If the crystals are now treated with colourless concentrated nitric acid, barium nitrate, virtually insoluble in nitric acid, is precipitated leaving a solution of periodic acid. The suspension is kept at 60 – 70°C. with constant stirring for an hour, cooled to 30°C. and filtered through a fritted-glass Buchner funnel. The filtrate is evaporated under reduced pressure, filtered if necessary from any further precipitate of barium nitrate, and further concentrated as above A 90 – 96% yield of very pure paraperiodic acid is obtained in this way.[1] The same acid can also be prepared by electrolytic oxidation of iodic acid at an anode of platinum coated with lead dioxide, the cathode solution being dilute nitric acid.[7]

When heated in vacuo at 80°C., paraperiodic acid is dehydrated to the dimeso-acid, $2H_5IO_6 = H_4I_2O_9 + 3H_2O$. At 100°C., further dehydration occurs and the meta-acid is formed: $H_4I_2O_9 = 2HIO_4 + H_2O$.[8]

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THE PROPERTIES OF PERIODIC ACID AND OF PERIODATES GENERALLY

Few physical properties of the colourless, crystalline periodic acids have been investigated. The vapour pressure of mesoperiodic acid at 85 and 100°C. is 7·5 and 10 mm. respectively. The vapour pressures of dimesoperiodic acid and metaperiodic acid at 85°C. are 5 and 3 mm. respectively.[1] The molar magnetic susceptibility of the para-acid was found to be $-71 \cdot 4 \times 10^{-6}$ c.g.s. units from which it was concluded that it is simply dihydrated metaperiodic acid, $HIO_4,2H_2O$.[2]

All the periodic acids are readily soluble in water and the solubility of the para-acid at various temperatures[3] is shown in Table XVI.

TABLE XVI. - SOLUBILITY OF PARAPERIODIC ACID IN WATER

Temperature, °C.	Solubility, % W/W.
0	77·91
20	78·57
25	78·74
33	79·32
35	79·50
37	79·66
40	80·30
45	80·78

From X-ray diffraction studies of periodic acid solutions it is concluded that a high degree of complexity and quasi-crystalline arrangement exists in periodate solutions.[4,5] From thermochemical data, the radius of the periodate ion in aqueous solution is calculated to be 2·49 A.[6]

Periodic acid exists in aqueous solution as the para-acid, H_5IO_6, which behaves effectively as a weak dibasic acid.[7] Using the cells,

$$\text{glass electrode} \left| \begin{matrix} NaH_4IO_6, \\ HNO_3 \end{matrix} \right| \begin{matrix} \text{saturated} \\ NaNO_3 \end{matrix} \left| Hg_2Cl_2 \right| Hg$$

$$\text{and glass electrode} \left| \begin{matrix} NaH_4IO_6, \\ NaOH \end{matrix} \right| \begin{matrix} \text{saturated} \\ NaNO_3 \end{matrix} \left| Hg_2Cl_2 \right| Hg,$$

and extrapolating the data to zero ionic strength, the first and second thermodynamic dissociation constants, K_1 and K_2, were obtained. By measuring the variation of these constants with temperature, the corresponding free energy, heat content and entropy changes were derived[8] and are given in Table XVII.

TABLE XVII. - THERMODYNAMIC PROPERTIES OF THE DISSOCIATION OF PERIODIC ACID

Temperature, °C.	10	20	30	40	50
$K_1 \times 10^3$	5·89	6·17	6·31	6·17	6·03
$K_2 \times 10^9$	9·77	9·77	9·55	9·12	8·51
ΔG_1° g.-cal.mole^{-1}	2890	2970	3060	3160	3290
ΔG_2° g.-cal.mole^{-1}	10380	10740	11100	11500	11900
ΔH_1° g.-cal.mole^{-1}	820	490	100	-340	-840
ΔH_2° g.-cal.mole^{-1}	180	-190	-630	-1130	-1670
ΔS_1° g.-cal.deg.$^{-1}$mole^{-1}	-7·3	-8·4	-9·7	-11·2	-12·8
ΔS_2° g.-cal.deg.$^{-1}$mole^{-1}	-36·0	-37·2	-38·8	-40·4	-42·1

The ionization of the para-acid has also been investigated spectrophotometrically and, from ultra-violet absorption measurements, the first and second dissociation constants were found to be $5 \cdot 10 \times 10^{-4}$ and $2 \cdot 0 \times 10^{-7}$ respectively at 25°C. In evaluating these constants, allowance was made for the dissociation $H_4IO_6^- \rightleftharpoons IO_4^- + 2H_2O$ which has an equilibrium constant of 40 at 25°C.[9] This equilibrium was apparently not considered in the potentiometric work and is almost certainly responsible for the difference between the two sets of results. These determinations may be further complicated by the dissociation $2H_3IO_6^{--} \rightleftharpoons I_2O_9^{4-} + 3H_2O$. Certainly both $K_2H_3IO_6$ and $K_4I_2O_9,9H_2O$ may be crystallized from the same solution.[9] The pH values of various potassium mesoperiodate solutions have been determined and indicate[10] that a significant degree of hydrolysis of the mesoperiodate ion occurs according to the equation, $HIO_5^{--} + H_2O \rightleftharpoons H_2IO_5^- + OH^-$. The third, fourth and fifth ionization constants of paraperiodic acid are very small. Nevertheless, all five hydrogen atoms are replaceable when a sparingly soluble salt such as Ag_5IO_6 is formed. The electrical conductances of aqueous potassium metaperiodate solutions at 25°C. have been determined[11] and some data are given in Table XVIII.

TABLE XVIII. - EQUIVALENT CONDUCTANCE OF POTASSIUM METAPERIODATE SOLUTIONS

Molality	0·020421	0·010570	0·005778	0·0033106
Equivalent conductance	115·67	118·75	120·99	122·51
Molality	0·0015560	0·00072096	0·00049401	
Equivalent conductance	124·20	125·36	125·71	

These figures lead to a value of 127·90 ± 0·07 $ohm^{-1} cm^2 mole^{-1}$ for the limiting equivalent conductance of potassium metaperiodate and 54·38 ± 0·07 $ohm^{-1} cm^2 mole^{-1}$ for the limiting conductance of the metaperiodate ion.[11] The standard oxidation-reduction potential of the iodate-periodate system, $IO_3^- + 3H_2O \rightarrow H_5IO_6 + H^+ + 2e^-$ was found[12] to be approximately 1·5 V. The measured potential of the system in N-H_2SO_4 solution was found to be 1·375 V. and in aqueous solution at pH 9·5, 0·706 V.[13] The exchange of iodine or oxygen atoms between separate periodate ions has been shown to be very small.[14] In the reduction of periodate ions at the dropping mercury electrode, two distinct waves are observed, the first corresponding to reduction to iodate and the second to reduction of iodate to iodide.[15] Thus, traces of periodate in iodates may be determined.[61]

The reaction between periodates and iodides in acid solution has been reinvestigated. In the presence of excess of iodide, the complete reaction is $IO_4^- + 7I^- + 8H^+ \rightarrow 4I_2 + 4H_2O$, and this proceeds at room temperature at a rate given by

$$-d[IO_4^-]/dt = [IO_4^-][I^-](1{\cdot}3 \times 10^3 F_1 + 1{\cdot}4 \times 10^7 F_2[H^+]^2)$$

where F_1 and F_2 are coefficients dependent on the total ionic concentration.[17] The first step in this reaction is the intermediate formation of iodate;

$$IO_4^- + 2I^- + H_2O \rightarrow IO_3^- + I_2 + 2OH^-.$$

When radioactive iodide is used, the iodine produced is also active but the iodate remains completely inactive showing that it is produced entirely from the inactive periodate.[18]

Paraperiodic acid in the solid state or in sulphuric acid solution reacts vigorously with fluorine. Hydrogen fluoride, oxygen and some fluorine monoxide, F_2O, are evolved from two simultaneous reactions:

$$H_5IO_6 + 2F_2 \rightarrow O_2 + 4HF + HIO_4 \text{ and}$$

$$H_5IO_6 + 4F_2 \rightarrow 2F_2O + 4HF + HIO_4.$$

The resultant metaperiodic acid was not isolated because further dehydration by the fluorine tends to occur. By passing sufficient fluorine over solid paraperiodic acid, iodine pentoxide was obtained. At temperatures above 250°C., the reaction proceeds even further and iodine pentafluoride is formed.[19]

Periodates react with hydrogen peroxide and oxygen is evolved:

$$IO_4 + H_2O_2 \rightarrow IO_3^- + H_2O + O_2.$$

The reaction is autocatalyzed by iodate ions and a steady reaction rate may be achieved by the preliminary addition of a small quantity of iodate; too much added iodate retards the reaction considerably.[20] Hydrogen sulphide when passed into aqueous periodic acid solution is oxidized partly to sulphate and partly to free sulphur:

$$6H_5IO_6 + 15H_2S \rightarrow 3I_2 + 2H_2SO_4 + 13S + 28H_2O.$$

Excess hydrogen sulphide reacts further with the iodine to form hydriodic acid and more free sulphur.[21] Thiosulphates in slightly acid solution are oxidized by periodic acid to a mixture of tetrathionate and sulphate:[22]

$$HIO_4 + 8Na_2S_2O_3 + 7HCl \rightarrow 4Na_2S_4O_6 + NaI + 7NaCl + 4H_2O;$$

$$HIO_4 + Na_2S_2O_3 + H_2O \rightarrow HI + 2NaHSO_4.$$

The reduction of periodate to iodate by arsenious acid or arsenites, $IO_4^- + AsO_3^{3-} = IO_3^- + AsO_4^{3-}$, was found to be a bimolecular second order reaction, with a reaction velocity constant at 25°C. of 5·5 mole^{-1} litre sec.$^{-1}$ The reaction rate is relatively insensitive to the hydrogen ion concentration between pH 3 and 7.[23]

Tellurium dioxide dissolves in concentrated periodic acid, and if the solution is evaporated in a vacuum desiccator the addition product $2TeO_2,HIO_4$ is isolated: when heated this decomposes to tellurium dioxide and iodine.[24]

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THE PREPARATION AND PROPERTIES OF THE METAL PERIODATES

Lithium diparaperiodate dihydrate, $Li_8I_2O_{11},2H_2O$, has been prepared by passing a brisk current of chlorine through a boiling lithium hydroxide solution of iodine.[1]

It was convenient to consider the preparation of sodium para- and metaperiodates in relation to that of periodic acid (see page 896). Below 34·5°C., three stable salts crystallize from the system $HIO_4-NaOH-H_2O$, namely, sodium metaperiodate trihydrate, $NaIO_4,3H_2O$, disodium paraperiodate, $Na_2H_3IO_6$, and trisodium paraperiodate, $Na_3H_2IO_6$. Above 34·5°C., the trihydrate is not stable and anhydrous sodium metaperiodate may be crystallized directly from aqueous solution.[2] The *X*-ray diffraction patterns of both the anhydrous[3] and trihydrated[4] sodium metaperiodate have been examined. The anhydrous salt has a tetragonal structure[3] with four molecules in the unit cell;[5] the space group of the structure is C^6_{4h}.[5,6] The *a* parameter has been determined very precisely and has the value 5·3222 ± 0·0004 A. From the spacing of the layer lines the *c* parameter was found to be 11·93 A. On this basis the I–O distance is 1·792 A. and the O–O distance 2·67 A.[6] The compressibility of sodium metaperiodate has been determined using pressures up to 25,000 kg. per sq. cm.[7] The fractional decrease in volume with applied pressure is given in Table XIX, together with the corresponding data for some other periodates.

TABLE XIX. - COMPRESSIBILITY OF PERIODATES

Applied pressure kg per sq. cm.	$\Delta V/V_0$			
	$NaIO_4$	KIO_4	$RbIO_4$	NH_4IO_4
2000	0·0078	0·0079	0·0093	0·0081
5000	0·0184	0·0190	0·0219	0·0195
10000	0·0336	0·0355	0·0400	0·0368
15000	0·0436	0·0497	0·0553	0·0524
20000	0·0569	0·0617	0·0685	0·0664
25000	0·0658	0·0820	0·0809	0·0791

The specific and molar susceptibilities of disodium paraperiodate were found to be $-0{\cdot}257 \times 10^{-6}$ and $-69{\cdot}9 \times 10^{-6}$ c.g.s. units respectively.[8]

Potassium periodate can be prepared by any of the general methods already described (see page 896). The details of its manufacture on an industrial scale in the United States[9] and in Russia[10] have recently been given. In the former case, crude potassium iodate in caustic potash solution at 105°C. is treated with excess of chlorine. More potassium hydroxide is then added to the hot solution, which on cooling deposits crystals of the dimesoperiodate, $K_4I_2O_9$. This salt is then digested at 105°C. with commercial nitric acid and the solution evaporated to half its volume and allowed to crystallize. Potassium metaperiodate separates and is washed with distilled water, drained centrifugally and dried in an oven; this first crop of crystals represents a yield of approximately 75%. Potassium periodate crystallizes with a tetragonal structure, the *a* and *c* parameters being 5·75 and 12·63 A. respectively.[5] Its compressibility[7] is given in Table XIX. Only two salts crystallize from the system $HIO_4-KOH-H_2O$, namely, anhydrous potassium metaperiodate, KIO_4, and the hydrated dimeso- salt, $K_4I_2O_9,9H_2O$ or $K_2H_3IO_6,3H_2O$, the temperature of transition to the anhydrous form being 78°C.[2] Potassium metaperiodate is slowly soluble in water at room temperature, up to 3 weeks being necessary for saturation to be reached.[11] Its solubility in water and in various salt solutions has been determined on several occasions[2,11,12] together with the corresponding activity coefficients.[11,12] The most recent value for the solubility of potassium metaperiodate in water at 25°C. is 0·02248 molal, in which solution the mean molal activity coefficient is 0·866.[11] The electrical conductance of potassium periodate solutions is recorded in Table XVIII (see page 899). The ternary system $KBF_4-KIO_4-H_2O$ has been investigated at 35°C. but no evidence of double salt formation was obtained.[13] The dimesoperiodate can be obtained in a very pure state and is a useful standard in acidimetry. It reacts quantitatively with strong acids, $K_4I_2O_9 + 2HCl \rightarrow 2KCl + 2KIO_4 + H_2O$, the equivalence point being easily detected by any normal acid-base indicator such as methyl-orange. This salt has the advantage of possessing a conveniently high molecular weight.[14]

Rubidium and cæsium periodates have been prepared and their crystal structures investigated.[3,15] The former has a tetragonal,[3] the latter an orthorhombic structure, the unit cell dimensions being:-[15]

	a_0(A.)	b_0(A.)	c_0(A.)
Rubidium periodate	5·874 ± 0·003		12·938 ± 0·007
Cæsium periodate	5·838 ± 0·003	6·014 ± 0·003	14·364 ± 0·007

The compressibility of rubidium periodate[7] is given in Table XIX.

Anhydrous ammonium metaperiodate crystallizes in colourless tetragonal crystals.[3] The space group of the structure is C_{4h}^6 and there are 4 molecules in the unit cell,[16] the dimensions of which are a_0 = 5·983 ± 0·003 A. and b_0 = 12·790 ± 0·007 A.[15] Its compressibility[7] is also given in Table XIX. Ammonium trihydrogen paraperiodate, $(NH_4)_2H_3IO_6$, crystallizes with hexagonal symmetry in the space group C_{3i}^2. The unit cell dimensions are a_0 = 6·88 ± 0·005 A. and c_0 = 11·10 ± 0·05 A. The $[IO_6]^{5-}$ group consists of oxygen atoms arranged octahedrally around the iodine atom, probably distorted by the hydrogen bonds. The I-O bond distance is 1·93 A.[17] The heat capacity of diammonium trihydrogen paraperiodate passes through a maximum at approximately 254°K.[18] At a similar temperature, i.e., in the temperature range 246° to 255°K., its dielectric constant, ϵ, indicates a marked transition from a strongly polarized high-temperature form to a low temperature modification with a small dielectric constant. For example, ϵ at 20°C. is 178, at -20°C. is 40 and at -80°C. is 10. The specific conductivity varies in a similar manner. Both principal axes of the crystal (perpendicular and parallel to the *c* axis) were investigated but no anisotropy was detected. The transition is thought to be due to a rearrangement of the hydrogen bonds in the crystal although little structural change or lattice expansion was observed from the Laue photographs above and below the transition temperature. This behaviour is not shown by the corresponding sodium salt, which has a dielectric constant of 50 almost independent of temperature, or by any metaperiodates which have very low dielectric constants.[19,20]

Further details of the preparation of silver periodates have been given. Silver metaperiodate, $AgIO_4$, can be prepared by mixing at 40-50°C. potassium metaperiodate and silver sulphate solutions in concentrated sulphuric acid.[21] Alternatively, potassium metaperiodate may be added to a solution of silver perchlorate in concentrated nitric acid at room temperature. In each case, yellow crystalline silver periodate separates.[21] In less strongly acid solution silver trihydrogen paraperiodate, $Ag_2H_3IO_6$, can be prepared in almost 100% yield by mixing at the lowest possible temperature a solution of potassium metaperiodate in dilute nitric acid with aqueous silver nitrate. Under these conditions, a very pure product is obtained.[22] Silver mesoperiodate, Ag_3IO_5, is prepared by adding excess of silver nitrate to hydriodic acid solution, followed by a large excess of potassium persulphate. The solution is boiled until the precipitated silver iodide redissolves. It is then cooled and neutralized with ammonia solution, when brown silver mesoperiodate is precipitated.[23]

All the silver periodates are sparingly soluble in water. The solubility of silver trihydrogen paraperiodate at 25°C. is 1·65% and that of the mesoperiodate 0·25% at 18°C.[22] When an aqueous solution or suspension of silver trihydrogen paraperiodate is warmed, a mixture of the mesoperiodate, Ag_3IO_5, and silver paraperiodate, Ag_5IO_6, is formed. With continued heating the mixture is transformed almost completely into the paraperiodate. If silver trihydrogen paraperiodate is warmed to 60°C. in dilute nitric acid, a reddish-brown precipitate of secondary silver mesoperiodate, Ag_2HIO_5, is formed. With concentrated acids all the silver periodates are transformed into silver metaperiodate.[22]

The ternary system periodic acid–silver oxide–water has been investigated at 0°C. by mixing silver oxide with dilute periodic acid solution and stirring the solution for 3 – 4 days with purified CO_2-free air. The saturated solution and wet residue were then analysed and three compounds were isolated, viz., (i) white crystalline silver metaperiodate dihydrate, $AgIO_4,2H_2O$, (ii) straw-yellow silver dimesoperiodate trihydrate, $Ag_4I_2O_9,3H_2O$, and (iii) black crystalline silver paraperiodate, Ag_5IO_6. The compound Ag_5IO_6 is stable in water up to 35°C.; $Ag_4I_2O_9,3H_2O$ is not, but is stable in the presence of dilute periodic acid, whilst $AgIO_4,2H_2O$ is stable only in concentrated periodic acid solutions ($\nless$ 52% I_2O_7).[24]

Silver metaperiodate is a yellow crystalline solid of density 5·57 g. per c.c. It forms tetragonal crystals, isomorphous with sodium periodate,[3] belonging to the space group C_{4h}^6 with 4 molecules in the unit cell, the dimensions of which are $a_0 = 5{\cdot}368 \pm 0{\cdot}02$ A. and $c_0 = 12{\cdot}013 \pm 0{\cdot}03$ A.[21] Silver trihydrogen paraperiodate crystallizes with rhombohedral symmetry in the space group C_{3i}^2. The unit cell contains one molecule and has the dimensions $a_0 = 5{\cdot}31$ A. and $\alpha = 67°38'$.[25,22] Its density is 5·50.[22]

Silver trihydrogen paraperiodate is structurally similar to the corresponding ammonium salt and shows the same anomalous behaviour with respect to specific heat[18-20,26] and dielectric constant.[19,20] Its molal heat capacity has been measured[26] from 15° to 300°K. and some smoothed results are shown in Table XX.

TABLE XX. - MOLAR HEAT CAPACITY OF SILVER TRIHYDROGEN PARAPERIODATE, $Ag_2H_3IO_6$.

Temperature, °C.	Cp, g.-cal.deg.$^{-1}$mole.$^{-1}$	Temperature, °C.	Cp, g.-cal.deg.$^{-1}$mole.$^{-1}$
15	2.000	224	56.33
20	3.540	227.25	63.5 (max.)
25	5.216	230	58.89
30	6.879	234	52.04
50	12.68	238	48.08
100	22.57	250	43.49
200	38.24	260	44.26
220	48.61	300	47.48

The heat capacity is seen to pass through a maximum at 227·25 ± 0·20°K. The change in heat content for this transition is 358·1 ± 20·0 g.-cal.mole.$^{-1}$ The corresponding entropy change is 1·60 ± 0·10 g.-cal.deg.$^{-1}$mole^{-1}; and this agrees well with the calculated value of 1·64 based on a hydrogen bond theory of transition. The entropy of crystalline silver trihydrogen paraperiodate at 298·19°K. was calculated as 59·44 g.-cal.deg.$^{-1}$mole^{-1}.[26] A change in dielectric constant was observed in the temperature range 210 – 240°K. but the change is not so marked as with the ammonium salt.[20] The specific and molar magnetic susceptibilities of silver trihydrogen paraperiodate are $-0{\cdot}2256 \times 10^{-6}$ and $-99{\cdot}66 \times 10^{-6}$ c.g.s. units respectively. The corresponding parameters for silver mesoperiodate are $-0{\cdot}233 \times 10^{-6}$ and $-123{\cdot}64 \times 10^{-6}$ c.g.s. units.[8]

In addition to the cupric periodates already described (Mellor, II, 412), a deep green paraperiodate heptahydrate, $Cu_5(IO_6)_2,7H_2O$, has been reported. It is prepared by drying at 45°C. the precipitate obtained when paraperiodic acid solution is added to dilute copper acetate solution. At 74°C. this heptahydrate slowly loses water forming the corresponding pentahydrate. The vapour pressures of the heptahydrate and pentahydrate at 74°C. were found to be 5 mm. and 3 mm. respectively.[27] Quaternary copper periodate has been prepared by adding a solution of disodium paraperiodate in dilute nitric acid to copper sulphate solution.[28] The yellowish green crystalline precipitate is paramagnetic with a molar susceptibility at 32°C. of $2387{\cdot}85 \times 10^{-6}$ c.g.s. units.[28]

The alkaline earth dimesoperiodates, $Ca_2I_2O_9,8H_2O$, $Sr_2I_2O_9,8H_2O$ and $Ba_2I_2O_9,4H_2O$ have been prepared by boiling a concentrated solution of a soluble salt of the metal with solid disodium paraperiodate.[29,30] To precipitate the strontium salt, prolonged boiling is necessary.[30] Zinc diparaperiodate, $Zn_4I_2O_{11},5H_2O$, can be prepared in the same way.[29] When slightly acid zinc acetate solution is added to a neutral iodate solution, white crystalline anhydrous zinc paraperiodate, $Zn_5(IO_6)_2$, is obtained.[31] In neutral solution this precipitation is quantitative and affords the basis of a proposed method of determining zinc.[32,33] Under similar conditions, cadmium paraperiodate, $Cd_5(IO_6)_2$, is also quantitatively precipitated.[33] The specific and molar magnetic susceptibilities of mercuric periodate were found to be $-0{\cdot}1828 \times 10^{-6}$ and $-225{\cdot}55 \times 10^{-6}$ c.g.s. units respectively.[8]

Aluminium metaperiodate dodecahydrate, $Al(IO_4)_3,12H_2O$, has been prepared by slowly adding a freshly precipitated aluminium hydroxide suspension to a 5% excess of cold solution of periodic acid. After filtration, the solution is concentrated on a water bath and then allowed to cool and crystallize. Octahedral crystals of the dodecahydrate separate which can be filtered off and dried. They are quite stable in air and are not hygroscopic. The existence of a trihydrate (Mellor, II, 415) could not be confirmed.[34] Aluminium diparaperiodate, $Al_2H_2I_2O_{11}$, was prepared by adding an aqueous aluminium sulphate solution to a suspension of trisodium paraperiodate and heating the mixture on a steam bath.[35] Thallic diorthoperiodate, $Tl_4I_2O_{13},3H_2O$, was obtained by digesting thallic oxide with concentrated sulphuric acid and adding a solution of trisodium paraperiodate in concentrated nitric acid. A yellowish-brown precipitate of the thallic periodate is slowly formed.[35] The specific and molar nagnetic susceptibilities of lanthanum mesoperiodate dihydrate were found to be $-0{\cdot}1591 \times 10^{-6}$ and $-60{\cdot}76 \times 10^{-6}$ c.g.s. units respectively.[8]

Yttrium, erbium and cerium, like all other rare earths, form mesoperiodates of the type MIO_5, usually with 4 molecules of water of crystallization. Yttrium also forms a diorthoperiodate, $Y_4I_2O_{13},11H_2O$.[36] Both yttrium and cerous mesoperiodates are paramagnetic, their specific susceptibilities at 32°C. being $9{\cdot}072 \times 10^{-6}$ and $5{\cdot}143 \times 10^{-6}$ c.g.s. units respectively.[28] Gadolinium mesoperiodate, $GdIO_5,4H_2O$, is reported to be very deliquescent.[37] Three basic indium periodates have been described, $2InIO_5,In(OH)_3,6H_2O$, $3InIO_5,In(OH)_3$, and $4InIO_5,In(OH)_3,5H_2O$. All are white crystalline compounds and all are converted by concentrated nitric acid into yellow crystalline indium mesoperiodate, $InIO_5$.[38]

In order to prepare titanium periodate, freshly precipitated titanium hydroxide is dissolved in nitric acid and added to a solution of trisodium paraperiodate also dissolved in nitric acid. On concentrating the solution the titanium periodate, $Ti_7I_2O_{21}$, or $7TiO_2,I_2O_7$, is precipitated.[39] Zirconium diorthoperiodate, $Zr_3I_2O_{13}$, can be obtained in the same way from zirconium hydroxide,[39] though there is some doubt as to whether the final product contains 14 or 17 molecules of water of crystallization.[39,40] Two other periodates of zirconium have been reported; zirconyl diparaperiodate $(ZrO)_4I_2O_{11},18H_2O$, prepared by mixing solutions of zirconium nitrate and potassium metaperiodate, and zirconyl diorthoperiodate, $(ZrO)_6I_2O_{13},20H_2O$, obtained by the action of paraperiodic acid on freshly precipitated zirconium hydroxide. This last salt was systematically dehydrated and distinct hydrates containing 13, 8, 6 and 4 molecules of water of crystallization were characterized. The anhydrous salt was also obtained.[40]

Ceric paraperiodate monohydrate, $CeHIO_6,H_2O$, is precipitated when acid solutions of ceric ammonium nitrate and trisodium paraperiodate are mixed. The anhydrous salt is obtained by drying the monohydrate in a vacuum.[39] If a slight excess of hot neutral potassium periodate solution is added to a hot neutral solution of thorium iodate, complete precipitation of the thorium as thorium paraperiodate pentahydrate, $ThHIO_6,5H_2O$, takes place. After standing 3 – 4 hours the gelatinous precipitate can be filtered off on a sintered-glass filter and dried at 110°C. to the pentahydrate. This procedure is suitable for the determination of thorium.[41] In acid solution, precipitation is slow and incomplete[39,41,42] and use is made of this fact to separate ceric cerium from thorium and the rare earths.[42] The precise details for the precipitation and determination of cerium as ceric paraperiodate monohydrate have been described.[42]

A basic stannic periodate, $4SnO_2,I_2O_7$, is precipitated when a solution of metastannic acid in nitric acid is added to trisodium paraperiodate also in nitric acid.[39] Plumbic diparaperiodate, $Pb_2I_2O_{11}$, can be prepared by dropwise addition of a solution of trisodium paraperiodate in 50% acetic acid to a cooled solution of freshly prepared, dry lead tetra-acetate in a minimum of glacial acetic acid. The compound is hydrolyzed in boiling water.[35]

Bismuth periodate is obtained by mixing solutions of potassium metaperiodate and bismuth nitrate in 50% acetic acid. The resulting precipitate is digested, washed by decantation with acetic acid, filtered, washed with warm water and dried at 100°C. The precipitate has a variable composition depending on the initial ratio of metaperiodate and bismuth concentrations; when these are equal, the final precipitate approximates to the formula: $Bi_5(IO_6)_3,4H_2O$, i.e., the paraperiodate.[43]

Manganese mesoperiodate, $Mn_3(IO_5)_2$, was prepared by quickly adding an ice-cold solution of manganous chloride to a thin paste of excess of silver mesoperiodate. After filtration through an ice-cold funnel, the solution was evaporated at less than 15°C. Pink crystals of the mesoperiodate formed after two days; they decomposed on warming to room temperature.[35] Complex periodates of quadrivalent maganese may be obtained as crystalline precipitates by the interaction of manganic acetate and a metal periodate in nitric acid solution. They all have the general formula $MO,2MnO_2,I_2O_7,xH_2O$ where M is any alkali metal, alkaline earth metal, silver, copper, inc, cadmium or lead.[44]

Ferric paraperiodate, $FeH_2IO_6,4H_2O$, was prepared by mixing a solution of trisodium paraperiodate in concentrated nitric acid with a concentrated solution of ferric chloride.[35] Ferric mesoperiodate, $FeIO_5,11H_2O$, is obtained by passing chlorine through a boiling suspension of ferric hydroxide and iodine.[45] A chromium periodate, $Cr_2O_3,2I_2O_7,22H_2O$, is obtained when chromic hydroxide and iodine are chlorinated together.[45]

Refs. p. 906

No cobalt periodate has been isolated from a mixture of disodium paraperiodate and cobalt sulphate solutions (Mellor, II, 416–417). However, cobalt diparaperiodate, $Co_4I_2O_{11},12H_2O$, can be obtained by mixing hot solutions of cobalt nitrate and potassium metaperiodate.[46] It is paramagnetic, its specific susceptibility at 32°C. being $23{\cdot}67 \times 10^{-6}$ c.g.s. units.[28] Several complex cobaltiperiodates have been described. They are prepared simply by adding potassium metaperiodate to a solution of cobalt nitrate and metal salt. Two types of complex salt are obtained: tetracobaltiperiodates derived from the acid containing Co^{III}, I, and H in the ratio 4 : 3 : 3 and monocobaltiperiodates, with Co^{III}:I:H equal to 1 : 1 : 2. Sodium, potassium, ammonium, silver and barium[47] tetra- and monocobaltiperiodates were prepared.

The preparation of nickel periodates has been reinvestigated. The light green precipitate obtained by mixing nickel sulphate and disodium paraperiodate solutions has been shown to be the para-salt, $Ni_5(IO_6)_2,13H_2O$, whereas the dirty green precipitate obtained from nickel chloride and potassium metaperiodate solutions has the composition $NiO,2I_2O_7,25H_2O$.[46] Nickel paraperiodate is also paramagnetic and its specific susceptibility at 32°C. was found to be $20{\cdot}744 \times 10^{-6}$ c.g.s. units.[28] Pale yellow uranyl dimesoperiodate, $(UO_2)_2I_2O_9$, is precipitated when cold solutions of uranyl nitrate and potassium metaperiodate are mixed; in hot solution, no definite compound is formed.[48]

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SECTION XXXVI

SPECTROSCOPY OF IODINE, HYDROGEN IODIDE, IODINE MONOXIDE AND IODINE OXY-ACIDS

By R. F. BARROW

THE IODINE ATOM: OPTICAL SPECTRA

References to work on the optical spectra of the iodine atom are summarized in Table I. Transitions involving the lowest states of the neutral atom have been recognized from experiments on the absorption spectrum of the heated vapour, and through excitation by active nitrogen. The spectrum of the neutral atom, and that of singly-ionized iodine, I^+, are now quite well known, but there is only fragmentary information about the higher spectra. Hyperfine structure in the arc and first spark spectra has been much studied: departures from the interval rules are interpreted in terms of quadrupole interactions.

TABLE I.- THE OPTICAL SPECTRA OF THE IODINE ATOM

Reference	Spectrum	Notes
1-7	I	atomic absorption
8	I	resonance fluorescence not shown by line 2062 A.
9,10	I	excitation by active nitrogen
11-14	I,II	excitation in discharges
15	I,II	wave-lengths: 2300 to 5235 A.
16,17	I	Schumann region: ground-state ^2P interval
18	I,II	wave-lengths: 800 to 1900 A.
19,20	I,II	wave-lengths: 2562 to 7468 A.
21	I	wave-lengths: 6965 to 9114 A. analysis
22	I	wave-lengths: 4765 to 9732 A. analysis
23	I	wave-lengths: 3200 to 9114 A. analysis
24	I	criticism of analysis[23]
25	I,II	Zeeman effect
26	I,II	wave-lengths: 750 to 2300 A. Zeeman effect: analysis
27,28	I,II	Stark effect
29	I-III	Zeeman, Stark effects
30-32	I-IV	wave-lengths: 2220 to 7350 A.
33	I	series: ionization potential
34	I,II	analysis: h.f.s.
35	II	classification: h.f.s.
36	II	wave-lengths: 1275 to 2376 A.
37	II-VIII	wave-lengths: 190 to 1009 A.
38	II	Zeeman effect: analysis: wave-lengths
39-42	III	classification
43	IV	wave-lengths: 2224 to 3547 A. classification
44	VI	classification
45	VII	classification
46	VIII	classification of lines between 190 and 202 A.

TABLE I (continued)

Reference	Spectrum	Notes
47	II	preliminary observations on h.f.s.
48	I	h.f.s. i = ?9/2
49,51	II	h.f.s. i = 5/2
50	I	h.f.s. i = 5/2 anomalous intervals
52,53	II	h.f.s. anomalous intervals
54	II	Zeeman effect in h.f.s. i = 5/2 nuclear quadrupole effects
55	II	h.f.s. nuclear quadrupole effects
56,57	II	h.f.s. nuclear quadrupole moment
58	I	h.f.s. nuclear quadrupole moment nuclear magnetic moment
59	I,II	nuclear quadrupole moment
60,61	II	h.f.s. quadrupole interaction

The lowest energy states of the neutral atom[34] are as follows:-

$5s^2\,5p^4\,6s$:	$^2P_{1/2}$	63186·49 cm^{-1}
	$^2P_{3/2}$	61816·17
	$^4P_{1/2}$	60892·67
	$^4P_{3/2}$	56089·33
	$^4P_{5/2}$	54630·00
$5s^2\,5p^5$:	$^2P_{1/2}$	7602·7
	$^2P_{3/2}$	0

The lowest ionization potential[34] is at 10·44 ev.: the second ionization potential[34,38] is at 19·26 ev. Properties of iodine nuclei[62] are as follows (see also page 912):-

Mass number	a.m.u.	spin	magnetic moment, n.m.	$Q(10^{-24}\text{cm}^2)$
127	126·9453	5/2	2·8090	-0·7
129	-	7/2	2·6181	-0·5

Lines at 3754·6, 4170·4 and 5369·7 A. have been suggested[63] as suitable for analytical purposes. The M.I.T. list[64] gives the following sensitive lines: 2062·38, 5161·188 and 5464·61 A. The excitation of lines has been discussed.[65] An atlas containing iodine spectra has been published.[66]

The possibility of an electron affinity spectrum of the iodine atom has been considered:[67,68] the maximum should lie at about 3000 A., but it is expected to be too feeble to be observed.[68]

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THE IODINE ATOM: *X*-RAY SPECTRA

Measurements in the *K*-series have been made in emission,[1-4] and the *K*-absorption edge has been studied.[5-7] The effect of chemical combination on the position of the edge has not been detected,[7] and the effect on the structure of the edge is very small.[5,7] Iodine itself shows a faint structure near the short wave-length side of the absorption limit, both in the solid and vapour states,[7] but again no shift is detectable. The relative intensities of the lines K_{α_1} and K_{α_2} have been measured for the fluorescent radiation.[8]

The *L*-spectrum has been the subject of a number of investigations,[9-18] and there is available fairly complete information about wave-lengths,[9-12,18] satellite lines[15,17,18] and energy-levels.[13,14,16,18] Values of ν/R for the energy-levels, referred to L_{III}, are given in Table II.[18]

TABLE II. - *X*-RAY ENERGY LEVELS FOR IODINE

K 2443·15	L_{I}	382·25	M_{I}	79·10	N_{I}	13·86	$O_{\text{II,III}}$ 0·38
	L_{II}	357·48	M_{II}	68·68	$N_{\text{II,III}}$	9·15	
	L_{III}	[335·78]	M_{III}	64·56	N_{IV}	3·88	
			M_{IV}	46·63	N_{V}	3·78	
			M_{V}	45·76			

The *L* absorption edges of iodine have also been studied.[14,19-23] The positions of the limits (Table III)[23] and the character of the fine-structure depend somewhat on the state of chemical combination.[20,21,23]

TABLE III. - *L* ABSORPTION EDGES FOR IODINE, X.U.

Substance	L_{I}	L_{II}			L_{III}		
I_2	2385·9	2547·7			2711·3		
NaI	83·0	46·4	2543·2		13·4	2708·7	
KIO_3	83·0	48·6	43·2		12·4	06·6	2698·3
KIO_4	82·6	47·9	42·8	2535·6	12·1	06·1	98·3

The emission of *X*-rays in the *L* series has been observed[24] in an electrodeless discharge. Relative intensities and widths of lines in the *L* series have been discussed in terms of the Auger effect.[25] Experiments on the scattering of *X*-rays by crystalline iodides have been described.[26-29,30] The magnetic spectra of the electrons emitted by iodides irradiated with *X*-rays have been studied.[31] The mass absorption coefficient for iodine crystals has been measured[32] at a wave-length of 59 *X.U.*, and an empirical method of calculating these coefficients has been proposed.[33]

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THE IODINE MOLECULE, I_2

ABSORPTION SPECTRUM OF GASEOUS IODINE

The banded absorption spectrum of iodine in the visible region attracted much attention,[1-3] even before the theoretical basis for its interpretation had been laid. It was in fact the analysis of Wood's resonance series (see page 916) which provided the key to the unravelling of the rotational structure of the absorption bands:[4] subsequent work has yielded improved values for the constants of this system,[4] now recognized as arising from a transition B $^3\Pi_{0_u^+}$–X $^1\Sigma_g^+$. A number of additional bands have been identified,[6-8] especially at the short wave-length end of the system,[6] where the bands converge to a limit beyond which there lies a region of continuous absorption. The last band-head to be measured lies at 20024·4 cm.$^{-1}$: the extrapolated position of the convergence limit is at 20037 cm.$^{-1}$ From the intensity alternation in the rotational lines of bands of this system, it was shown[9] that the nucleus ^{127}I obeys Fermi-Dirac statistics, and that the nuclear spin is 5/2. At higher pressures of iodine, a further band-system is observed in absorption[10] in the infra-red region, between 8300 and 9300 A., arising from a transition from the ground-state X $^1\Sigma_g^+$ to a feebly-bound upper state A $^3\Pi_{1u}$.

Absorption bands assigned to the iodine molecule are also observed in the quartz ultra-violet[11-16] and Schumann[17,18] regions. At low temperatures and pressures, bands are found[12,18] in the region 1700 to 2065 A. and between 1540 and 1770 A.[17,18] At higher temperatures and pressures, banded absorption may be seen at longer wave-lengths (2100 to 2760 A.);[11] at about 1000°C. continua are observed[13,14] with long wave-length edges at 3263 and 3427 A., and bands between 2974 and 3427 A., and between 2716 and 2880 A. A further band at 2670 A. has been observed[16] at 160°C. and 390 mm. pressure. It is then clear that there are a number of excited states reached from the ground state by absorption of ultra-violet radiation. There is still some doubt, however, about the analyses of these various systems. Attempts have been made to fit the large number of bands observed at low or moderate pressures between 1900 and 2700 A. into a single system,[15,19] but the results are not entirely convincing.[20] Likewise, the analyses of the overlapping systems at shorter wave-lengths are doubtful.[20,21] A systematic study of these bands with adequate resolution is overdue.

The B - X system has been the subject of a number of other investigations. The magnetic rotation spectrum (the spectrum of the light transmitted through crossed nicols when the magnetized gas is placed between the prisms in such a way that the light travels along the field) was first observed by Wood and Ribaud.[22] In the case of the alkali metals, results both elegant and fruitful

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are obtained in this experiment, but this is not so for iodine,[23] although the behaviour is in qualitative agreement with the theoretical treatments.[24,25] The results of an interferometric study[26] of the effect of a magnetic field on the absorption at 5461 A. have been discussed.[27]

In early interpretations, the possibility that spectral limits were to be identified with ionization processes was often considered.[28] Franck[29] first gave the correct interpretation of the absorption limit (ca. 4990 A.), namely that it corresponds to the process:-

$$I_2 \rightarrow I(^2P_{3/2}) + I(^2P_{1/2}).$$

Thus the dissociation energy[30-33] of the molecule is equivalent to 20037 cm.$^{-1}$, less the separation $^2P_{1/2} - {}^2P_{3/2}$, 7603 cm.$^{-1}$, in the ground state of the iodine atom. This is equivalent to $D_0''(I_2) = 35{\cdot}542 \pm 0{\cdot}020$ kg.-cal./mole, in excellent agreement with the value obtained from the measurement of the pressure in partly dissociated iodine gas,[34] 35·514 ± 0·050 kg.-cal./mole.

The state B $^3\Pi_{0^+}$ lies above the dissociation limit to normal atoms, and it might be expected that it should be possible to observe predissociation in this state by interaction with repulsive states correlating with the normal atoms. This is indeed the case, and Turner[36] has shown by the direct observation in absorption of the production of atomic iodine, that light of wave-length greater than 5100 A. is capable of inducing predissociation in the presence of argon. This collision-induced predissociation has also been demonstrated by the apparent increase in intensity of the absorption bands with $v' > 12$ in this system on the addition of oxygen or nitrogen.[37,39,40] According to Turner,[36] the maximum effect occurs at $v' \sim 25$: Kondrat'ev and Polak[40] found three maxima, at $v' = 22, 29$ and 39, which they attribute to three different unstable electronic states. The decrease in life-time in the predissociated upper levels has been demonstrated by an increase in the line-breadths in the presence of oxygen or nitrogen.[38] These effects are further confirmed by the results of experiments on the quenching of the iodine fluorescence (see page 920) and by the weakening of the B–X system in emission[20] when iodine is excited in presence of a foreign gas.

An increase in pressure through photo-dissociation with visible light has been reported.[35] The iodine line at 2062 A. has been observed in fluorescence[41,42] on illuminating iodine vapour with light of wave-length about 1400 A. The absorption in molecular beams has been studied.[43]

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IODINE MOLECULE: INTENSITY OF ABSORPTION

Qualitative experiments[1,11] on the variation with temperature of the intensity of absorption by iodine vapour in the visible region of the spectrum have been followed by a number of measurements[2,5,6,10] of the extinction coefficient. Earlier measurements[2] between 4500 and 6000 A. have been criticized,[5] and it has been suggested that the apparent failure of the gas[2] to obey Beer's law arises from some surface phenomenon,[3] but according to Luck,[9] the effect, which occurs in the region of banded absorption, is an experimental one, arising from the use of inadequate spectral resolving power. Certainly the observed shape of the extinction curve near the maximum at low pressures and temperatures (Fig. 1) is unusual, and would suggest the existence of two overlapping transitions, were it not that the curve assumes the normal Gaussian shape at higher temperatures and pressures.[5,10] Measurements at 4358 and 5461 A. confirm this effect:[4] in the banded region at 5461 A. the addition of helium raises the extinction coefficient, while in the region of continuous absorption (4358 A.) the addition of helium leaves its value unchanged. Thus it may be concluded that the main absorption band ($\nu_{max} \sim 19000$ cm^{-1}) represents a single transition whose true shape is Gaussian. In the usual way, this band becomes broader with increasing temperature,[7,8,10] and the value of ϵ_{max} decreases. The characteristics of this band in the gas are not very different from those observed for the violet solutions of iodine in inert solvents[5,6,10] (Figs. 1 and 2; see pages 915 and 925) at the same temperature, but the value of the extinction coefficient is a little lower in the gas: thus, ϵ_{max} at 300°C. is calculated[10] to be 685 for the gas, and in presence of inert gas[5] this figure is raised to about 820 as compared with 920 for carbon tetrachloride solution (see page 924).

Both violet solutions and the gas show a second very weak maximum[10] at about 14200 cm^{-1}

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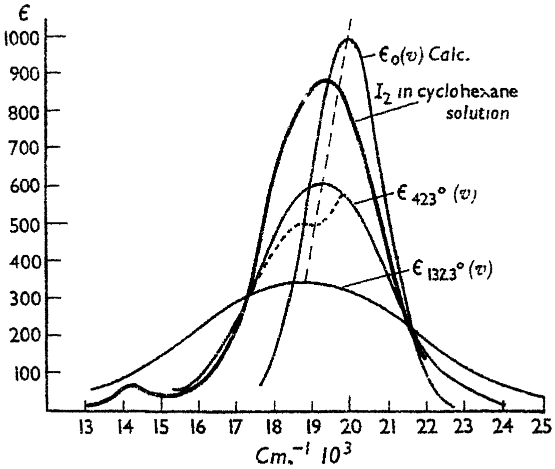

Fig. 1. COMPARATIVE REPRESENTATION OF THE ABSORPTION SPECTRUM OF I_2 AT T = 0°K. (CALC.; POSITION OF MAXIMUM IS ASSUMED); T = 423°K., 1323°K. AND AT 291°K. IN SOLUTION

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IODINE MOLECULE: EMISSION SPECTRUM

The emission spectrum of iodine has been much studied, but there remain a number of observations yet to receive satisfactory interpretation. In earlier work, attention was paid to the conditions of spectral excitation,[1-5,8,9,12,18] and to the question of the identity of the emitter of the spectrum.[1,2] The suggestion that certain features were to be interpreted as an electron-affinity spectrum[7,11] has been disproved.[15,17] The simplest part of the spectrum is the band-system B - X at λ > 4990 A., which may be excited in many ways: the system does not, however, appear in emission in presence of a considerable pressure of inert gas[31] (see page 913). This system also appears in emission from hot iodine vapour (t > 450°C.).[10,22] Under these conditions there also appears the only continuum in iodine which seems definitely to be established, at λ < 4990 A. (the convergence point of the B - X system), and this is considered[10,17] to be the recombination continuum arising from the process:-

$$I + I^* = I_2 + h\nu.$$

With this exception, what are described in the earlier literature as continua, appear on closer examination to consist of diffuse overlapping bands.[14,17,20] These diffuse bands have been observed in the region between about 2000 and 5000 A. Often strongly emitted both in discharges[5,19,21] and in flames[13] is a group near 3460 A. The problem of deriving unambiguous analyses of systems

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of closely-spaced diffuse bands, arising from transitions between states in which the molecule has very different equilibrium configurations, is a difficult one, but progress has been made by examining the emission spectra in the presence of quite high pressures (several hundred mm.) of inert gas.[27-29] Under these conditions, the molecules approach thermal equilibrium in the vibrational levels of the upper electronic states: they populate therefore a smaller number of initial vibrational levels than is normal in a discharge tube, and the number of bands observed is thereby reduced. This simplified spectrum may be more readily analysed. Transitions D↔X, F→X and E→B (see Table IV, page 923) have been treated successfully in this way.[27,30,32] Other systems of diffuse bands appear to arise from transitions between stable upper states and repulsive lower states.[23,24,26,30] Plausible interpretations[31] of these transitions have been given, but many of the assignments await confirmation.

A high-frequency discharge through iodine vapour has been suggested as a source of continuous radiation[25] in the region 1950 to 3000 A.

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IODINE MOLECULE: FLUORESCENCE SPECTRUM

The fluorescence spectrum of iodine was the subject of the classical investigations of Wood,[1,2,52] much of whose work was done before the development of the theoretical treatment of the spectroscopy of diatomic molecules. When iodine vapour is illuminated with monochromatic light, e.g. Hg 5461 A., it emits a fluorescence spectrum which consists, according to the conditions of excitation, of a series of lines (Wood's resonance series) or of bands. The problem of identifying the emitter prompted investigations of the effect of

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temperature[3] on the fluorescence and of ionization potentials in the fluorescing vapour.[4] The basis for the interpretation of the resonance series was laid by Lenz:[5,6] subsequent theoretical progress,[14,16] together with the experimental work of Mecke,[10,11] who correlated measurements on the fluorescence and absorption spectra, prepared the way for the analysis of both spectra by Loomis.[18] If iodine vapour at not too high pressure is illuminated with Hg 5461 A. as excited in a cold lamp giving sharp lines, only one resonance series, consisting of doublets[41] of nearly constant separation, is obtained. No anti-Stokes lines are observed for this series, so that the first doublet has $v'' = 0$. Loomis[18] was able to show that the mercury line under these conditions overlaps appreciably with only one[42] iodine absorption line, the line $R(33)$ of the 26,0 band of the B – X system. The main resonance series then consists of the doublets $R(33)$, $P(35)$ of the progression $(26,v'')$: this series has now been observed[17,29,49,50] as far as $v'' = 38$. If J_r is the J-value for the upper state, then the doublet separation may be written:-[2,50]

$$\begin{aligned}\Delta\nu &\equiv R(J_r - 1) - P(J_r + 1)\\ &= (4J_r + 2)[B_e - \alpha(v'' + \tfrac{1}{2}) - D_e(2J_r^2 + 2J_r + 2)].\end{aligned}$$

Interferometric measurements[49,50] of the wave-lengths of many of the lines of this series have led to the determination of the molecular constants for the ground state of the iodine molecule with high accuracy (see Table IV, page 923): the values derived are in good agreement with those determined from the rotational analysis[18] of the absorption bands.

If the line exciting fluorescence is broad enough to cover more than one absorption line, further series are developed:[1,8,10] analyses of several of these have been given.[2,19,52] Variations in intensity with temperature in some of these series, especially in anti-Stokes lines, have been studied.[7-9,30-34] The re-absorption of the fluorescent radiation has also been examined.[37] A rough comparison[40] shows that the iodine fluorescence is some three hundred times stronger than that of bromine.

Light of wave-lengths falling in the absorption continuum at $\lambda < 4990$ A. does not of course excite any fluorescence in iodine vapour, but the series excited by a number of other lines[15,20,27,31,34] at longer wave-lengths, e.g. Cd 5086, Cu 5218, Hg 5771, Hg 5792, Ne 5852, Na 5893 A., have been studied.

If the 5461 A. spectrum of iodine is examined when the vapour is in presence of ‘an atmosphere of helium at a pressure of only 2 or 3 mm. instead of in a high vacuum, the complete band spectrum, very similar to that excited by white light, appears in addition to the resonance spectrum, while at a pressure of 8 or 10 mm. the resonance spectrum disappears entirely and is replaced by the band-spectrum.’[1] Iodine molecules, raised to the state $J' = 34$, $v' = 26$ of B $^3\Pi_{0_u^+}$ by the absorption of radiation, suffer collisions with helium atoms in which there is an exchange of energy, so that molecules about to fluoresce are not now restricted to the single state reached by absorption, but may also find themselves in states with neighbouring J' or v' values (see also page 919). The details of this process are interesting.[22,24,25] It is found that every other rotational line in the resonance-collision spectrum is missing. As has been seen, the state $J' = 34$ is reached on absorption: this is an anti-symmetric level, as are all the levels with even values of J' in B $^3\Pi_{0_u^+}$. The lines found in the resonance-collision spectrum all correspond to even values of J', and the lines with odd values of J' are missing. It thus appears that transitions between symmetric and anti-symmetric levels do not occur to any extent during collisions. (In the absorption spectrum, both sets of lines occur, since there exist iodine molecules in both symmetric and anti-symmetric states: however the selection rule sym $\not\leftrightarrow$ anti holds for the absorption, or emission, process).

Excitation of iodine vapour by light of wave-length between about 1800 and 2600 A. also leads to fluorescence series,[12,13,21,26,28,35,36,38,39,44-47] but the phenomena here are a good deal more complex than in the case of the visible series. Pringsheim[52] gives an excellent summary of the facts. Many of the observations can be understood if it is supposed that there is an excited state of relatively high dissociation energy, but with an equilibrium internuclear distance considerably greater than for the ground state. The existence of several excited states combining with the ground state to give transitions in the ultra-violet region is of course established from the experiments on the absorption spectrum. At low temperatures, fluorescence may be excited only by short wave-length radiation[12] ($\lambda < 2100$ A.), but as the temperature is raised, higher vibrational levels in the ground state become populated, and fluorescence can be excited, for example, by Hg 2537 or 2654 A. at 600°C.[21,35,36,45,46] Very long doublet series have been observed in emission from discharge-tubes under certain conditions:[39,44] these series are excited by the iodine lines at 1830 and 1846 A. produced in the discharge itself. Two of these series have been followed as far as the 96th members, and thus provide information about the spacing of the vibrational levels in the ground state at high values of v''.

In addition to these various resonance series, which appear to raise no very difficult problems apart from the identification of the upper states involved, there may also appear sets of apparently diffuse bands (McLennan bands) throughout the region between 2000 and 4800 A.[12,13,21,35,36,38,46] In spite of a great deal of work, a convincing interpretation of all these bands has yet to be put forward, although two systems, D-X and F-X have now received satisfactory analyses.[48,53]

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IODINE MOLECULE FLUORESCENCE: LIFE-TIME AND QUENCHING

Observations on the edge of a defined beam of fluorescent vapour lead to an upper limit for the life-time of the excited state leading to the visible fluorescence of iodine:[1] the value obtained was $t < 10^{-6}$ sec. Measurements[4] with a Kerr cell give $t = (1{\cdot}0 \pm 0{\cdot}1) \times 10^{-8}$ sec. This is somewhat shorter than would be expected,[29] for the transition $B\ {}^3\Pi_{0+} - X\ {}^1\Sigma^+$ is partially forbidden: moreover the high sensitivity of iodine to self-quenching has been interpreted on the assumption of a relatively long life-time.

The fluorescent radiation of iodine is partly polarized.[30] If the visible fluorescence is excited by linearly polarized white light, it is found that the degree of polarization of the fluorescent radiation is about 14%, in agreement with theoretical prediction:[23,29] the degree of polarization does not vary much with temperature at constant pressure.[2] It is reduced by collisions in which the orientation of the molecular axis is changed: this effect has been studied by Mrozowski,[23,24] who found that the efficiency of foreign gases in promoting depolarization increases with their mass. He has also studied the effect of a magnetic field on the degree of depolarization. A difference between the polarizations of the R and P lines of a resonance doublet arises if they are excited by circularly polarized light and viewed longitudinally. If, for example, the R line coincides with the exciting line, the value of J'' is the same before and after the absorption and emission processes, whereas for the P line there is a change from J'' to $J'' + 2$. In this case, the R line should show circular polarization of nearly 100%, while the P line should show much smaller polarization, and in the opposite sense: this effect has been verified.[19] A relatively high degree of polarization has been found for the McLennan bands.[16,17,29]

Two effects may occur on adding foreign gas to fluorescing iodine vapour: (i) there may be collisions in which energy is transferred between the iodine molecule and the foreign gas, so that instead of a series of sharp lines, the fluorescence spectrum now consists of bands (see page 917); (ii) the fluorescence may be quenched. Helium exerts a rather weak quenching action on the visible fluorescence of iodine, and its effect at low pressures is mainly to distribute iodine molecules among new vibrational and rotational levels in the upper state.[21] The transfer of energy in collisions with the other rare gases,[21] and with hydrogen and nitrogen[10-12] has been studied. The probability of transfer of rotational energy seems to be about the same as for vibrational energy: the vibrational changes are largely restricted to the range $\Delta v' = \pm 2$, with $\Delta v' = \pm 1$ somewhat more probable. There is little difference between the probabilities of the processes $v' = 26 \rightarrow 27$ or 25 or of $v' = 26 \rightarrow 28$ or 24. The effective diameters for these collisions are much greater (up to 25 times) than the kinetic theory cross-sections. They are also much larger than the cross-sections obtained from measurements of supersonic dispersion: this suggests a dependence on vibrational quantum number, for it has been found that molecules raised to $v'' = 1$ in X $^1\Sigma_g^+$ survive several thousand collisions with other iodine molecules before losing their vibration.[26]

The effect of a quenching gas on the intensity of fluorescence often follows the Stern-Volmer law:-[1]

$$I = I_0/(1 + kp)$$

where I is the intensity of fluorescence at quenching gas pressure p and I_0 is the intensity in the absence of quencher: k is a constant for a reaction pair. Iodine however is a strong self-quencher, and the effects of self-quenching and of quenching by foreign gas are not additive.[9] Moreover the value of k varies not only from one substance to another, but also with the wave-length. The quenching of the visible fluorescence by hydrogen,[10-12,25,27] nitrogen,[10-12,25,27] oxygen,[4,9,25,27] argon,[5-7,9,15,25,27] other rare gases,[9] chlorine[28] and benzene[20] has been studied. The following values[29] of the pressure required to reduce the value of I to $0{\cdot}5I_0$ illustrate the findings:-

Quenching gas	$p_{½}$, mm.	Quenching gas	$p_{½}$, mm.
Helium	70 (red region)	Hydrogen	5
	20 (green region)	Oxygen	3·5
Argon	6 (red region)	Ether	0·3
	2·3 (green region)	Chlorine	0·2
		Iodine	0·08

In the case of benzene, the Stern-Volmer law is not obeyed:[20] the results can be explained if it is assumed that at least two excited states are formed from the primary excited state on collision.

The quenching action seems quite definitely to proceed by collision-induced predissociation.[13] Iodine atoms have been detected[5-7] in absorption following illumination of iodine-argon mixtures with light of wave-lengths greater than 5100 A. (*i.e.* > 4990 A., the convergence limit in B $^3\Pi_{0^+}$), and the decreased lifetime in the upper state on addition of nitrogen or argon has been demonstrated by an interferometric study of the line breadths.[18] Finally, the quantum yield for the photo-dissociation process $I_2 + h\nu \rightarrow I + I$ has been measured[22] in mixtures of iodine with helium, argon, hydrogen and nitrogen at different wave-lengths (*a*) in the continuum at $\lambda < 4990$ A., (*b*) in the banded region near 4990 A., (*c*) in the banded region more remote from 4990 A. If the quantum yield in region (*a*) is 1·00, it is found to be 1·14 in (*b*) and 1·10 in (*c*), showing that all excited iodine molecules dissociate by collisions with foreign molecules. The quenching action is therefore practically never the dissipation process:-

$$I_2^* + X = I_2 + X,$$

but is nearly always the dissociation:-

$$I_2^* + X = I + I + X.$$

This dissociation process usually occurs at about the first kinetic collision of an excited iodine molecule with a foreign molecule: in helium, however, about ten or more collisions are necessary. The kinetics of the recombination of iodine atoms have been studied.[30] Measurements of the quantum efficiency of the fluorescence have been made:[28] the efficiency is independent of the wave-length between 5000 and 6500 A.

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IODINE MOLECULE FLUORESCENCE: MAGNETIC QUENCHING

The phenomenon of the quenching by a magnetic field of the fluorescence of iodine vapour in the visible region was discovered by Steubing.[1] Oldenberg[3] found that a magnetic field is without apparent effect on the blue fluorescence, and disproved[4] suggestions made to explain[2] the quenching in the visible region. Turner[5] studied the quenching action in its dependence on the wave-length of the exciting light: there is no quenching for an exciting wave-length of 5853 A., maximum quenching at about 5460 A. and decreasing quenching as the wave-length is decreased to 5085 A. Turner considered that this behaviour suggested a magnetically-induced predissociation, an idea which was fully confirmed by the theoretical work of Van Vleck,[6] who showed that the effect arises through a depopulation of the levels of the upper state 0_u^+ (correlating with I $^2P_{3/2}$ + I $^2P_{1/2}$) by interaction with a repulsive state 0_u^- (correlating with I $^2P_{3/2}$ + I $^2P_{3/2}$).[13] In the absence of a magnetic field, this predissociation is forbidden, but in the presence of a field, the two states mix to an extent depending on the field-strength. If Q is the ratio of intensities of a given line in the presence of a magnetic field H and in the absence of the field, then $Q = bH^2/(a + bH^2)$, where a and b are constants. This theoretical prediction[6] has been verified in studies[8-12] of lines excited by Hg 5461 A. in fields of up to 42600 gauss. A detailed examination of the combined effects of magnetic and collision quenching[7] revealed that they are not additive:

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it is as though the fluorescent molecule in presence of a magnetic field shows an enhanced collisional cross-section for quenching.

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IODINE MOLECULE: SPECTROSCOPIC CONSTANTS

The constants for those electronic states of the iodine molecule which appear to be established beyond doubt are collected in Table IV. Detailed theoretical work on the nature of the electron configurations in these states has been carried out by Mulliken[9-16] and by Van Vleck.[17] The problem of the nature of the upper state B, which had been supposed to be $^1\Sigma_u^+$, was resolved when it was shown[9-12,17] in fact to be $^3\Pi_{0_u^+}$, or more properly, 0_u^+. Later work[13] has given a very complete account of the theoretical expectations for the excited states both of the iodine molecule and of the molecule-ion, I_2^+. The lowest (vertical) ionization potential corresponding to the process:-

$$\sigma^2\pi^4\pi^4,\ ^1\Sigma_g^+ \rightarrow \sigma^2\pi^4\pi^3,\ ^2\Pi_{g,u}$$

is predicted to be 11·16 ev.: this is the average value for the two $^2\Pi$ states and the observed value is likely to be somewhat smaller, for $^2\Pi_g$ should lie below $^2\Pi_u$. The internuclear distance in the ground state of I_2^+ is expected to be about the same as for the ground state of I_2. The absolute intensities of the long-wave-length absorption bands have also been studied theoretically.[14-16] The experimental findings, namely that the $^3Q_1 \leftarrow N$ absorption with $\lambda_{max} = 7320$ A. is very weak, that $Q_0 \leftarrow N$ with $\lambda_{max} = 5200$ A. is strong, and that $^1Q \leftarrow N$ must be a weak transition buried under the much stronger continuum and bands of the $Q_0 \leftarrow N$ transition, are anomalous and it appears that this is to be attributed to a tendency towards case-c coupling in the iodine molecule. A strong V $(^1\Sigma_u^+) \leftarrow N$ transition is expected in the ultraviolet region. V is probably one of the states found in absorption near 56000 cm.$^{-1}$ (see page 912). Empirical correlations between the binding and the spectrum have been discussed.[20]

An accurate potential-energy function for the ground state of iodine has been constructed[18] using experimental values of the constants D_e, ω_e, $x_e\omega_e$, B_e and α_e: this curve lies somewhat above the Morse curve, the maximum correction to the latter being about +3 kg.-cal. The use of other potential functions has been considered.[19]

Thermodynamic properties of gaseous iodine have been calculated from spectroscopic data.[21,22]

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TABLE IV.- CONSTANTS FOR THE ELECTRONIC STATES OF THE IODINE MOLECULE

State	T_0	ω_e	$x_e\omega_e$	Transition	Reference
F ($^3\Pi_u$)	47147·5	96·7	0·49	F→X	3
E ($^1\Sigma_g^+$)	41355	102·2	0·34	E→B	1
D ($^1\Sigma_u^+$)	33291·6	104·0	0·2	D↔X	3
B $^3\Pi_{0u}^+$	15598·3	128·0	0·834	B↔X	1
A $^3\Pi_{1u}$	11803	44·0	1·01§	A←X	1
X $^1\Sigma_g^+$	0	214·248	0·6074*		2,3

§ $+0{\cdot}008\ (v+\tfrac{1}{2})^3$.

* $-1{\cdot}30 \times 10^{-3}\ (v+\tfrac{1}{2})^3 - 5{\cdot}529 \times 10^{-6}\ (v+\tfrac{1}{2})^4 - 1{\cdot}45 \times 10^{-7}\ (v+\tfrac{1}{2})^5$.

State	B_e	α_e	D_e	r_e	Reference
B $^3\Pi_{0u}^+$	0·02920	$1{\cdot}7 \times 10^{-4}$ §		3·016 A.	1
X $^1\Sigma_g^+$	$0{\cdot}03736_4$	$1{\cdot}206 \times 10^{-4}$	$4{\cdot}55 \times 10^{-9}$	2·667	2

§ further terms known.

Notes: A number of states exist with $T_0 > 50000$ cm.$^{-1}$: their analyses do not however appear to have been established with certainty.[1,3,4,5]

The value for r_e'' is in fair agreement with those obtained by electron diffraction, $r'' = 2{\cdot}66$ A.[6] and 2·674 A.[7,8]

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THE ABSORPTION SPECTRUM OF IODINE IN SOLUTION

The problem of the colour of iodine solutions has attracted much attention. In typically inert solvents, such as carbon disulphide and carbon tetrachloride, the colour is violet, like that of the vapour, whereas in oxygenated solvents such as alcohol and ether, the colour is brown.[7] Solutions in benzene are of an intermediate, red, colour. A summary of the earlier literature relating to these solutions is given in Table V. In some cases, complications arise through the reactivity of iodine with the solvent, as for example, with water, alcohol and acetone, where absorption by small amounts of tri-iodide ion[5,6,7,19,34,44] may obscure the iodine absorption.

TABLE V.- VALUES OF λ_{max} AND OF ϵ_{max} FOR IODINE IN VARIOUS SOLVENTS

Solvent	Reference	λ_{max}, A.	ϵ_{max}
Carbon disulphide	1,2,7,12,13,20,25,31	5185	1172
Carbon tetrachloride	5,7,10,12-14,17,20-22,24-26,31	5170	918
Stannic chloride	22	5120	
Titanic chloride	22	5200	
Arsenic trichloride	22	(4800)	
Chloroform	1,2,7,17,25,31	5110	880
Methylene chloride	17	5020	840
Dichloroethane	17	5000	850
n-Propyl chloride	17	4950	865
n-Butyl chloride	17	4950	840
cis-Dichloroethylene	17	5100	900
trans-Dichloroethylene	17	5150	940
Ethylene trichloride	31	5150	960
Ligroin	4		
n-Hexane	7,12,20	5250	940
cyclo-Hexane	29	4900	1010
Benzene	1,2,7,13,14,16.21,25,26,31	5000	1040
Toluene	1,7,14,16,31	4970	1020
Xylene	1,14	4960	1070
Substituted benzenes	7,30		
Pyridine	7	4800	(530)
Water	5,7.8,18-21	4700	(640)
Methyl alcohol	13,14,20,21,25,26	4380	995
Ethyl alcohol	1,2,6,7,13,14,16,23,26,27	4470	995
iso-Propyl alcohol	7,13	4380	1110
tert.-Butyl alcohol	14		
Acetic acid	13	4780	775
Acetic anhydride	7		
Acetone	7,14,25	(4600)	(500)
Ether	2,13,16,29	4560	1034
Dioxan	29,31	4515	940
Iodine vapour		5200	820

The dispersion of iodine solutions in the visible region,[3] the infra-red transmission of a carbon tetrachloride solution,[24] and the effect of temperature on the absorption of solutions,[4,6,23] have been studied. With a solution of iodine in alcohol,[27] the absorption maximum shifts by about 1300 cm^{-1} to shorter wave-lengths on cooling to 20°K.: the shift is interpreted as a solvent-cage effect. Attempts have been made to correlate the solution spectra with those obtained in the gas phase.[9,11] Rabinowitch and Wood[20,21] have measured the extinction coefficients of strongly illuminated solutions of iodine. Usually, the extinction coefficient decreases on illumination, by photo-dissociation of the iodine molecules into atoms, but solutions in benzene, methyl alcohol and water show reversible increases in extinction on illumination. Benzene solutions were studied in detail: the observations can be explained in two ways involving, on illumination, either (i) the destruction of complexes, C_6H_6,I_2, or (ii) the formation of new absorbing complexes, C_6H_6,I or C_6H_6,I_2.

Several ideas have been invoked to explain the varying colours of iodine solutions: it has been suggested that the brown solutions contain colloidal particles,[15] solvated molecules,[14,29] or associated molecules,[12] and the correlation with dipole moment has been stressed.[17,28,30] The existence of molecular complexes has been suggested,[11] and a theory of solvent-solute interaction in terms of the cage theory of solutions has been put forward.[49-52] However, the work of Benesi and Hildebrand[32,33] on solutions of iodine in benzene and other aromatic solvents for the first time demonstrated rather conclusively the existence of 1:1 complexes of the type Ar:I_2. Previously little attention had been paid to the ultra-violet absorption of these solutions. Benesi and Hildebrand showed that they possess an intense absorption band near 3000 A. which is attributable neither to the solvents nor to iodine (see Fig. 2). By following the changes in the intensity of absorption with concentration, using an inert solvent, it was shown that the new band arises from a 1:1 complex. The extinction coefficient for the absorption by the complex may be determined, and thence the equilibrium constant for its formation. The original method of calculation of these constants has been improved:[35] characteristics of the benzene-iodine system are as shown below Fig. 2.

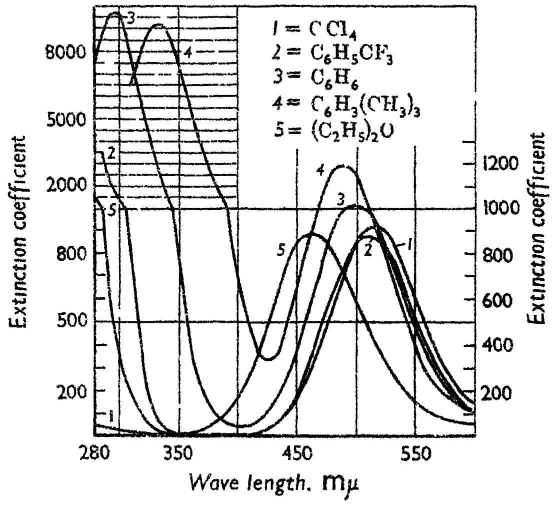

Fig. 2. ABSORPTION OF IODINE IN VARIOUS SOLVENTS

The ultra-violet absorption band is seen to be more significant than the visible absorption spectrum, which, except in the case of certain oxygenated solvents (see Table V), is seldom very different either in position or in intensity from the vapour spectrum. Indeed, some of the changes in colour as between different solvents are to be attributed less to shifts in the iodine absorption band than to changing overlapping of the ultra-violet bands on to the violet end of the visible spectrum.[33]

Visible absorption: λ_{max} = 5000 A.; ϵ_{max} = 1040.
Ultra-violet absorption: λ_{max} = 2970 A.; ϵ_{max} = 14000
Equilibrium constant for the formation of the complex benzene-I_2
(mole-fraction units): 2·3, in pure benzene;
1·9, in infinitely dilute benzene in carbon tetrachloride.
Heat of formation of complex: −1·45 kg.-cal./mole in pure benzene.

These conclusions, based on observations on solutions of iodine in benzene, toluene, *o*- and *p*-xylenes and mesitylene,[33] all of which appear to form complexes, and on trifluoromethylbenzene, which does not do so, have been confirmed and extended in later work. Further measurements on the benzene complex have been made,[36] from which it appears that in addition to the main complex band at 2970 A. there may be a weaker band at about 2600 A. (although it is difficult to disentangle this from the benzene absorption) which is of some theoretical interest.[54] The spectra of solutions of iodine with naphthalene in carbon tetrachloride solution have also been studied:[41] values obtained are K = 2·66, ϵ_{max} = 7250, λ_{max} = 3600 A., f (oscillator strength) = 0·21. The complex is thus somewhat stronger than is that with benzene. The absorption spectrum of the complex appears to be determined much more by the aromatic partner than by the halogen.

The spectra of solutions in unsaturated aliphatic solvents and other donor solvents may also be interpreted in terms of complex formation: experimental results are given in Table VI.

TABLE VI.- NON-AROMATIC IODINE COMPLEXES

Donor molecule	λ_{max}: visible	λ_{max}: ultra-violet	K	Reference
*cyclo*Hexene	4900 A.	3020 A.	3·4	42
Di-*iso*butylene		3000	3·7	39
1-Bromo-1-propene	5050	2780	0·53	42
cis-Dichloroethylene	5100	2620	0·32	42
trans-Dichloroethylene	5150	2620	0·24	42
Trichloroethylene		2700	0·19	39
Tetrachloroethylene		2770	0·11	39
Acetic acid	4780		3·4	43
Dioxan	4515	2650	9·2	37,38

A detailed study[37,38] of the iodine-dioxan system from measurements on the bands both at 4515 and at 2650 A. leads to the following values for the formation of the complex:-

$$K\ (25°\text{C.}) = 9{\cdot}2 \text{ (mole fraction units)}$$
$$\Delta H = -3{\cdot}5 \text{ kg.-cal./mole}$$
$$\Delta S = -6{\cdot}7 \text{ e.u./mole}$$

Molecules with which complexes do not appear to be formed include trifluoroacetic acid,[43] sulphuric acid[43] and hydrogen fluoride.[44]

The infra-red spectra of some iodine solutions have been examined[45-48] with the aim of throwing light on complex formation. Observations on mesitylene solutions[45] have not been confirmed:[46,48] significant effects were found in the case of pyridine,[47,48] although detailed agreement between the two investigations is lacking, and whereas the earlier work[47] was interpreted as failing, except in the case of pyridine, to support the idea of the formation of complexes, in the latter[48] it is found that there occur small shifts in the position of certain solvent bands as would be expected if the solvent behaved as an electron-donor to the iodine molecule. The biggest effects occur when the solvent donor action is attributable mainly to a particular atom. In certain cases, as with pyridine and the picolines, the spectral changes are more considerable, and it is thought that here the action may proceed to the formation of ionic molecules,[48,54] $[(C_5H_5N)^+I][I^-]$ or ions $[(C_5H_5N)^+I]$ and $[I^-]$.

Reference has been made above to some of the ideas brought forward to explain the behaviour of iodine solutions. The view that 1:1 complexes are formed was not everywhere accepted, even after the work of Benesi and Hildebrand, and Bayliss and Rees[49-52] have stressed the possible effects on the spectrum, arising from the cage of solvent molecules surrounding the iodine molecule. For example, Rees[50] has given an interpretation of the shift of the visible absorption band of iodine dissolved in water as compared with the spectrum in the vapour phase, and Bayliss[52] has suggested that the intense band at 2900 A. found in benzene solution is to be regarded as the V,N transition in iodine vapour at 1800 A., shifted to longer wave-lengths. However, the view that the effects are to be ascribed to complex-formation, already strongly suggested by the experimental evidence, has been further supported by the theoretical work of Mulliken.[53-55] He has considered the aromatic complexes[54] in terms of resonance between a predominant no-bond structure (Ar,X_2) and small admixtures of ionic structures of the type $(Ar^+ - X_2^-)$. The strong, charge-transfer, spectrum results from a jump from this ground state of the complex to a predominantly ionic state, $(\mathrm{Ar}^+ - \mathrm{X}_2^-)$: the spectrum is thus characteristic of the complex. Not only does the observed position of the spectrum fit with this interpretation, but there is also agreement as good as can be expected between the observed and calculated intensities: thus for C_6H_6,I_2, $f = 0{\cdot}30$ (observed), $0{\cdot}19$ (calculated).

Useful reviews[56-59] of this subject have been published.

In the far ultra-violet region, extinction coefficients have been measured[36] for solutions of iodine in n-heptane. There is an intense broad band with $\epsilon_{\max} = 15000 \pm 2000$ and $\lambda_{\max} = 1880$ A., considerably stronger than the visible absorption band of iodine. It is suggested that this band arises from the expected transition ${}^1\Sigma_u^+ - {}^1\Sigma_g^+$ (V,N), although its broadness indicates that more than one transition may be involved. The observed oscillator-strength, $f = 0{\cdot}3 \pm 0{\cdot}1$, is smaller than that expected theoretically.

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STARCH-IODINE COMPLEXES

The absorption spectra of starch-iodine complexes have been studied,[1-4] especially with the object of elucidating the compositions of the starches. The visible absorption bands lie at somewhat longer wave-lengths than does the band in gaseous iodine, and are far more intense. The following figures[4] show how the bands vary for different amyloses:-

Amylose	Number of glucose residues	λ_{max}	ϵ_{max}
Potato	500	6280 A.	43000
Corn	250	6180	40400
Crystalline	175	6050	40100
Synthetic	85	5900	32900
Amylodextrin	44	5800	25400

Murakami[5] considers that the iodine forms a complex with the amylose oxygen, and that the intense absorption spectrum is of the charge-transfer type: according to his interpretation, the iodine in the complex is in the form of small units, $I_4^=$. (See also page 842).

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ABSORPTION SPECTRUM OF IODINE CRYSTALS AND OF ADSORBED IODINE

The absorption spectrum of thin layers of solid iodine has been examined. Bovis[1-3] found that there is a broad band in the ultra-violet with $\lambda_{max} \simeq 2550$ A., and that at longer wave-lengths there is a suggestion of a weak band near 5000 A. The phenomena are complicated however by the pleochroism[2] of the crystal, and rather different results were obtained by Hilsch and Pohle,[4] who found that the solid showed a single broad absorption band with a flat peak between 3000 and 4600 A., and decreasing absorption for $\lambda < 3000$ A. At low temperatures,[5,6] the crystals become red in colour, and at 20°K., they show absorption with $\lambda_{max} \sim 4750$ A., $\lambda_{max} \sim 5520$ A. (very weak), and continuous absorption in the ultra-violet.

Depolarization factors and extinction coefficients for iodine sols have been measured[7] between 2500 and 7000 A. It is concluded that the particles are spherical.

The absorption spectra of iodine adsorbed on various crystals have also been examined:[8-11] that of iodine on chabasite[8] is similar to the spectrum of gaseous iodine, with a strong maximum at 4975 A., but with stronger absorption at shorter wave-lengths and subsidiary maxima at 4375 and 3950 A. The spectrum on calcium fluoride[9] is strongly displaced to the violet as compared with the gaseous spectrum, and resembles rather the spectrum of the tri-iodide ion. The absorption maxima lie at 2830 and 3420 A., and the intensity is about 10^3 times greater than that for gaseous iodine. A discussion of these observations in terms of potential energy surfaces has been given.[9] The pure quadrupole spectrum of solid iodine has been studied.[12]

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HYDROGEN IODIDE

The elucidation of the structure of the infra-red spectra of the gaseous hydrogen halides was a most important step in the development of molecular spectroscopy.[1-5] Measurements of lines of the pure rotation spectrum of hydrogen iodide were made by Czerny,[6] from which he deduced a value for the internuclear distance in the gaseous molecule. The transition J $1 \leftarrow 0$ in deuterium iodide has now been observed in the microwave region.[7,8] Nuclear quadrupole effects split the line into three components,[9] from whose separation the coupling constant, eQq, may be obtained. Burrus and Gordy[8] obtain $eQq = -1823 \pm 1$, $B_0 = 97537{\cdot}2$ Mc./sec. The value of the coupling constant may be interpreted in terms of the ionic character and hybridization in the bond[7-9] (see also page 636).

The vibration-rotation spectrum of hydrogen iodide was first studied by Nielsen and Nielsen,[10] who analysed the $1-0$ and $2-0$ bands. Later, the $4-0$ band was photographed by Naudé and Verleger,[11] and the $1-0$ band studied with high resolution by Boyd and Thompson.[12] The value of α obtained in the latter work may be used to derive B_e for hydrogen iodide from the microwave value for deuterium iodide: this gives $B_e = 6{\cdot}512_9$ cm.$^{-1}$, in good agreement with the value obtained by Boyd and Thompson, but substantially lower than the earlier values. The spectroscopic constants for the hydrogen iodide molecule are collected in Table VII.

The vibrational Raman effect[13] in gaseous hydrogen iodide shows a broad

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TABLE VII.- SPECTROSCOPIC CONSTANTS FOR HYDROGEN IODIDE

ω_e	2309·53 cm^{-1}	B_e	6·512$_9$ cm^{-1}	r_e = 1·608$_8$ A.
$x_e\omega_e$	39·73	α_e	0·175	
		D	2·$_0$ × 10^{-4}	

Note: The vibrational constants are those of Naudé and Verleger:[11] they lead to $(\nu_0)_{1\text{-}0}$ = 2230·07, whereas the value observed[12] is 2229·60 cm^{-1}

line with maximum at 2216 cm^{-1}, and a long wave-length edge, near to $Q = 0$, at 2233 cm^{-1}, in good agreement with the infra-red value, ν_0 = 2229·6 cm^{-1}

The infra-red[14] and Raman[15] spectra of condensed hydrogen iodide have also been examined. As the following figures show, the frequency drops with decreasing temperature, at the same time, the structure of the Raman lines becomes increasingly difficult and complex.

TABLE VIII.- THE FUNDAMENTAL VIBRATION FREQUENCY FOR HYDROGEN IODIDE IN GASEOUS, LIQUID AND SOLID STATES

State	T, °K.	ν, cm^{-1}	Reference
gas	290	2230	12
liquid	226	2165	15
solid	217	2160	15
solid	145	2156	14
solid	120	2142	14
solid	85	2124	14

The importance of measurements of absolute intensities in infra-red spectra has been stressed by Mulliken:[16] results for hydrogen iodide have been given by Bartholomé.[17] However, Bartholomé's intensities, like those for the other hydrogen halides, are probably too low.[18] The emissivity of hydrogen iodide in the infra-red region has been considered.[19]

The ultra-violet absorption spectrum of gaseous hydrogen iodide has been discussed by a number of writers.[20-30] Absorption may be detected[23,24] at wave-lengths as high as 4000 A., so that here the process must be a dissociation into ground-state atoms, H($^2S_{1/2}$) + I($^2P_{3/2}$). However, since there is no sharp cut-off of the absorption on the low-frequency side, deductions about the value of the dissociation energy drawn from a supposed long-wave-length limit[24,27] are invalid.[26] Measurements of the extinction coefficient have been made over a short range of frequencies for both hydrogen and deuterium iodides.[25] The latter spectrum is shifted to somewhat higher frequencies as compared with the hydrogen iodide spectrum through a zero-point energy effect. The most extensive sets of measurements are those of Goodeve and Taylor[26] (27000 to 45000 cm^{-1}) and of Romand[28-30] (42800 to 67030 cm^{-1}); they are in good agreement (see Fig. 3). The maximum of the continuous absorption band lies at 2150 A. (46500 cm^{-1}); at shorter wave-lengths, discrete bands appear superimposed on the continuum. The trends in the absorption continua of the hydrogen halides are made clear from the following figures:-

	HCl	HBr	HI
λ_{max}, A.	1535	1785	2150
ν_{max}, cm^{-1}	65100	56000	46500
ϵ_{max}	890	525	174

From the variation of extinction coefficient with wave-length, it is possible to trace the course of the upper-state potential energy curves.[26,29,30] It is concluded that the transition in hydrogen iodide is two-fold, consisting of (i) a

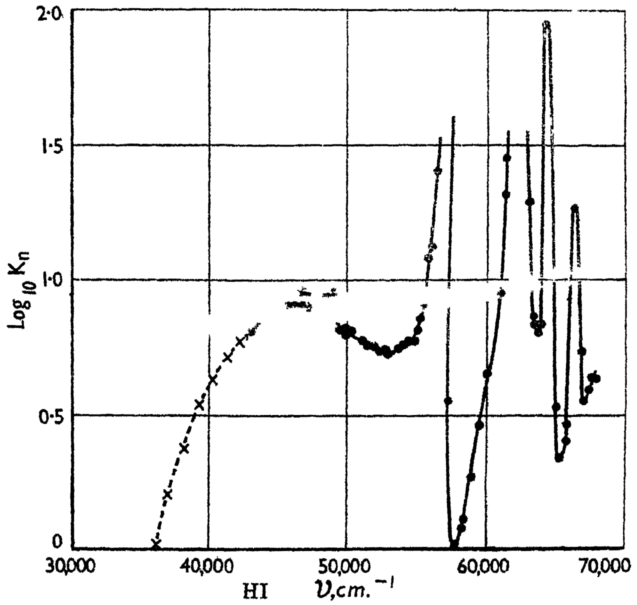

Fig. 3. RELATION BETWEEN $\text{LOG}_{10}K_N$ AND ν FOR HYDROGEN IODIDE

relatively weak transition, Q $^3\Pi_1 + {}^1\Pi_1 \leftarrow$ N, in which the upper-state complexes dissociate to give ground-state atoms, (ii) a stronger transition, Q $^3\Pi_{0+} \leftarrow$ N, where the upper state correlates with $H(^2S_{1/2}) + I(^2P_{1/2})$. These conclusions are in good agreement with the theoretical predictions of Mulliken.[31,32]

The absorption spectrum of hydrogen iodide at still shorter wave-lengths has been studied by Price.[33] The first strong absorption band lies at 1762 A.: it is the 0,0 band of a transition B$\leftarrow$X, analogous to those observed for hydrogen chloride and bromide. The corresponding transition C$\leftarrow$X is found at higher energies, the separation between B and C being related to the separation $^2\Pi_{1/2} - {}^2\Pi_{3/2}$ in the ground-state of the hydrogen iodide molecule-ion. Constants for these states are given below.

TABLE IX. - EXCITED STATES OF HYDROGEN IODIDE[33]

State[37]	$\nu_{0,0}$	$\Delta G_{1/2}$
C $(^2\Pi_{1/2})b\sigma$	62320	1970 cm.$^{-1}$
B $(^2\Pi_{3/2})b\sigma$	56750	-

In the region 1120 to 1350 A., there lies a Rydberg series of bands which converge on the state $(p\sigma)^2(p\pi)^3$, $^2\Pi_{1/2}$ of the molecule-ion by successive excitation of a non-bonding ($p\pi$) electron. Wave-numbers of the bands are given in Table X.

The lowest ionization potential of hydrogen iodide may then be obtained from the limit, 89130 cm.$^{-1}$, by subtracting the energy difference between the sub-states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ of HI^+. This separation has not yet been observed directly, but Price[33] gives reasons to show that it cannot be far from 5300 cm.$^{-1}$ The ionization potential becomes 10·39 e.v. or 239·9 kg.-cal. The predicted value[37] of the lowest 'vertical' ionization potential corresponding to

TABLE X.- RYDBERG SERIES IN HYDROGEN IODIDE[33]

n	$\nu_{obs.}$	$\nu_{obs.}-\nu_{calc.}$	n	$\nu_{obs.}$	$\nu_{obs.}-\nu_{calc.}$
2	74290	213	8	87700	20
3	81115	1	9	87960	-4
4	84200	38	10	88170	-2
5	85770	18	11	88325	-3
6	86700	15	12	88454	+4
7	87285	16	13	88540	-5

Note: The calculated values are with $\nu = 89130 - R/(n + 0{\cdot}70)^2$: subsidiary bands can be represented by:-

$\nu = 89130 - R/(n + 0{\cdot}93)^2$ and $\nu = 89130 - R/(n + 1{\cdot}25)^2$.

the process:-

$$\sigma^2\pi^4 \rightarrow \sigma^2\pi^3\ (^2\Pi_{3/2})$$

is 10·83 ev., in reasonable agreement with the experimental value.

The emission spectrum obtained from a discharge through hydrogen iodide vapour has been examined:[34,35] there appear continua with maxima at 3400 and 4280 A. These have been interpreted as arising from the hydrogen iodide molecule,[34,35] but it is not certain that this molecule is the emitter.[36]

The electronic states of hydrogen iodide have been treated in detail by Mulliken,[31,32] who has also made calculations of the absolute strength of the absorption continuum in the ultra-violet region. The experimental finding that most of the intensity is probably to be associated with the transition N → Q_0 does not correspond with the results of the theoretical calculations. The same anomaly occurs for methyl iodide and for iodine, and is probably to be associated with the importance of case-c coupling in the states of the iodine compounds.

The bond moment in hydrogen iodide has been calculated by an ionic-covalent resonance treatment.[39] An attempt has been made to establish a connexion between ionic character and ultra-violet absorption.[40] Potential energy functions for the ground state of the molecule have been investigated.[41,42] Relations between the force-constant and the internuclear distance have been discussed.[43,44] Fajans[45] considered the electron affinity of hydrogen iodide.

The dissociation energy of hydrogen iodide cannot be obtained directly from the present spectroscopic information about this molecule;[46,47] it is best determined from the values of the standard heat of formation of hydrogen iodide and the heats of dissociation of hydrogen and of iodine. Using values given in the Tables of the National Bureau of Standards,[48] there is obtained:-

$$D_0(\mathrm{HI}),\ 0^\circ\mathrm{K.} = 70{\cdot}48\ \mathrm{kg.\text{-}cal.}$$

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HYDROGEN IODIDE ION, HI$^+$

No spectrum attributable to the hydrogen iodide ion has yet been observed.[1,2] By analogy with the hydrogen chloride and hydrogen bromide ions, the ground-state should be ${}^2\Pi_i$, with $A \sim 5300$ cm^{-1} according to Price.[3] The value of $\Delta G''_{1/2}$ should be[2] about 2100 cm^{-1} The dissociation energy of the ion may be obtained from the cycle:-

$$D(\mathrm{HI}^+) = I.P.(\mathrm{I}) + D(\mathrm{HI}) - I.P.(\mathrm{HI}).$$

Using figures previously given:-

$$D_0(\mathrm{HI}^+),\ 0^\circ\mathrm{K.} = 71{\cdot}7\ \text{kg.-cal.}$$

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IODINE MONOXIDE, IO

A system of bands degraded to longer wave-lengths and lying in the region 4190 to 5800 A. was observed by Vaidya[1] in the emission spectrum of a coal gas–oxygen flame containing methyl iodide. He attributed the system to the molecule IO. Attempts to excite the bands in discharge tubes have not been successful,[2] but they have been obtained by adding iodine to the oxy-hydrogen flame.[3] The constants (cm^{-1}) derived from the vibrational analysis are given below: they support the identification of the emitter as IO.

State	T_e	ω_e	$x_e\omega_e$
A	21565	512	5
X	0	687	5

It is not certain that X is the ground-state. Extrapolation of the vibrational levels in X leads to the value 44 kg.-cal./mole for the dissociation energy.

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IODINE IONS AND ACIDS

THE IODIDE ION, I^-

The ultra-violet absorption spectrum of the iodide ion in aqueous solution has been studied by Fromherz and Menschick,[1] and at shorter wave-lengths, as far as 1800 A., by Scheibe.[2] The value of the extinction coefficient reaches 1 at about 2750 A.; the absorption increases at decreasing wave-lengths to maxima ($\epsilon \sim 13500$) at 2260 and 1940 A. The separation between the peaks is of the same order as the separation $^2P_{1/2}$ - $^2P_{3/2}$ in the ground state of the iodine atom. It has been stated that the absorption in the 2260 A. maximum does not follow the Lambert–Beer law exactly,[3] but there is no confirmation of this anomaly (see page 935). The spectrum is interpreted as a charge-transfer process[4,5,6] (see also page 655). The variation of the absorption with temperature and with solvent has been studied.[7]

The effect of potassium iodide on the absorption band of water at 0·77 μ has been studied.[8]

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THE TRI-IODIDE ION, I_3^-

The tri-iodide ion shows specific absorption in the ultra-violet region of the spectrum.[1-3] There are two maxima: figures for aqueous solution[3] are as follows:-

Refs. p. 935

λ_{max}, A.	ϵ_{max}
3530	26400
2875	40000

This does not appear to be a charge-transfer spectrum.[4] Concentrated aqueous solutions of potassium iodide show a variable absorption in the ultra-violet region through the formation of tri-iodide ion by air oxidation of iodide ion to iodine.[5] The tri-iodide ion spectrum varies somewhat with solvent[5] (see also page 924).

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INTERHALOGEN IONS, I_2X^-

The existence of ions of the type I_2X^- is suggested by the ultra-violet absorption spectra of solutions of iodine in aqueous sodium chloride and sodium bromide.[1]

Reference

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THE IODATE ION, IO_3^-, AND IODIC ACID, HIO_3

The iodate ion shows absorption in the quartz ultra-violet region. The value of the extinction coefficient in aqueous solutions of potassium iodate[1,2] rises from about 1 at 2900 A. to 1000 at about 2300 A.; the maximum has not been observed. The spectrum has been interpreted as a charge-transfer process (see page 655).

The Raman spectra of aqueous solutions of alkali-metal iodates have been studied.[3-6] The presence of four Raman shifts, together with the results of depolarization measurements,[6] indicate a pyramidal structure for the ion. The assignments of Shen, Yao and Wu[6] are as follows:-

	Species	ν cm.$^{-1}$	ρ
ν_1	A_1	779	0·43
ν_2	A_1	390	
ν_3	E	826	
ν_4	E	330	0·81

These conclusions are supported by studies of the infra-red spectra of the crystals.[7,8]

The Raman spectra of crystalline alkali-metal iodates have been examined.[3,4,9] Venkateswaran[5] has also studied the Raman spectrum of potassium biiodate, both in the crystalline state and in aqueous solution.

A number of observations of the Raman spectra of aqueous solutions of iodic acid at varying concentrations have been made,[3-5,10-14] but the interpretation of the rather complicated spectra is not certain. Hibben,[15] reviewing this work, concludes that the evidence indicates polymerization and a stepwise, incomplete, ionization in aqueous solution.

Refs. p. 936

The Raman spectrum of crystalline iodic acid has also been studied.[3,4,15-18] The earlier work is incomplete, for it has only recently been appreciated that the Raman spectrum of a crystal may depend on the orientation of the crystal with respect to the direction of illumination.[18]

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THE PERIODATE ION, IO_4^-

The Raman spectrum of crystalline potassium periodate, KIO_4, has been studied.[1,2] The strongest lines lie at 795 (10) and 842 (3) cm.$^{-1}$ The degenerate frequencies of the tetrahedral ion are split in the spectrum of the crystal, and Venkateswaran[2] observed 8 Raman shifts. His assignments for the fundamental frequencies of the ion are as follows:-

$$\nu_1:\ 795 \qquad \nu_3:\ 842\ \text{cm.}^{-1}$$
$$\nu_2:\ 286 \qquad \nu_4:\ 343$$

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PARAPERIODIC ACID, H_5IO_6

The ultra-violet absorption spectrum of aqueous solutions of paraperiodic acid shows a characteristic maximum at 2250 A. in the absence of interfering ions. The variation of the absorption with pH is interpreted[1] in terms of the equilibria:-

$$\begin{array}{lll} H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ & \qquad & K_1 = 2{\cdot}30 \times 10^{-2} \\ H_4IO_6^- \rightleftharpoons H_3IO_6^= + H^+ & & K_2 = 4{\cdot}35 \times 10^{-9} \\ H_3IO_6^= \rightleftharpoons H_2IO_6^{\equiv} + H^+ & & K_3 = 1{\cdot}05 \times 10^{-15} \end{array}$$

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SECTION XXXVII

THE ANALYTICAL DETERMINATION OF IODINE, IODIDE, HYPOIODITE, IODATE AND PERIODATE.

By L. A. HADDOCK

THE VOLUMETRIC ESTIMATION OF IODIDES

The volumetric determination of iodides follows in general the pattern outlined for chlorides or bromides, so that in most cases it is not possible to determine these ions, when present together, by any direct and simple titration. Many workers, however, have determined I^- in presence of Br^- or Cl^-, or both of these ions, by oxidizing the iodine to IO_3^- with chlorine, boiling off the bromine and excess of chlorine, and then allowing the iodate to react with potassium iodide in acid solution, whereby iodine equivalent to the IO_3^- and hence to the I^- originally present is liberated. The original method, attributed to Winkler, has subsequently been modified and subjected to numerous limitations. Thus, if chlorine is used for the initial oxidation and if bromides are also present, the magnitude of the error is proportional to the hydrogen-ion concentration at which the oxidation is performed. Bleaching powder is therefore recommended for the oxidation and succinic acid for the subsequent acidification, so that I^- may be determined in presence of 10 parts of Br^-.[1] To overcome the interference caused by the presence of excess of Br^-, a large excess of chlorine may be used for the oxidation, followed by the addition of potassium bromide and phenol to remove liberated bromine. The iodate produced may be titrated in the usual way with thiosulphate after the addition of potassium iodide and 20% phosphoric acid. Bromine or hypobromites may be used for the oxidation instead of chlorine.[2] The method may be modified by adding to 50 ml. of solution 25 ml. of acetone and enough 50% sulphuric acid to make the solution 2·5 N. in acidity, and then titrating with 0·1N-potassium iodate solution using starch paste as indicator. The titration is based upon the reaction

$$2HI + HIO_3 + 3C_3H_6O \longrightarrow 3C_3H_5IO + 3H_2O.$$

Under suitable conditions hydrochloric and hydrobromic acids are not oxidized.[3] The importance of establishing an optimum hydrogen ion concentration for accurate iodate-iodide titrations in presence of Cl^- or Br^- has been emphasised,[4] and it has been shown that with suitable precautions iodide may be determined directly in the mixed halides of photographic emulsions.[5] Titration with iodate may be carried out in presence of excess of hydrochloric acid. To about 0·5 g. of a metal iodide add 10 ml. of water and 40 ml. of hydrochloric acid (*d* 1·16) followed by 0·1N-potassium iodate (10·701 g. KIO_3/l) until most of the free iodine disappears. While the liquid is still brown, add 5 ml. of chloroform and shake after the addition of each drop of iodate solution until the pink colour in the chloroform disappears; the supernatant liquid is coloured bright yellow by iodine monochloride.[6] Alternatively, if excess of iodate be added to an iodide solution acidified with phosphoric acid, the liberated iodine may be boiled off and the residual iodate measured by adding potassium iodide and titrating the iodine then liberated.[7]

Further details, such as the necessity for buffering the solution suitably before measuring the IO_3^- formed by oxidation, have been discussed.[8,9] It has been observed that the liberation of iodine from an iodide–iodate mixture varies with the type and quantity of acid added.[10] In this connection it has also been noted that errors of about 0·5% are possible in dissolving iodine in alkali hydroxide and liberating the halogen again by means of acidification, and that with very weak solutions the error may even be as great as 5%.[11]

Another method proposed for the estimation of iodide is based upon the formation of cyanogen iodide which is less ionized than hydrogen cyanide.[12] In the presence of acid and an oxidizing agent, iodine reacts with hydrogen cyanide until it is completely converted into cyanogen iodide

$$I_2 + HCN \rightleftharpoons ICN + H^+ + I^-$$

An estimation of the quantity of iodine (or I^-) present may be based upon the volume of oxidizing solution required to effect the oxidation to cyanogen iodide, or since it reacts with thiosulphate as follows:

$$ICN + 2S_2O_3^{--} + H^+ \longrightarrow I^- + HCN + S_4O_6^{--}$$

the quantity of cyanogen iodide may be measured by titration with thiosulphate. Lang[12] describes a large number of variations of this type of titration. If the disappearance of the violet colour in carbon tetrachloride is taken as the end-point, 0·1 mg. of I^- may be titrated by this method with an accuracy of 1%.[13] Other modifications permit the direct determination of iodide in the presence of many heavy metals,[14] including iron.[15] The method is considered to be sufficiently accurate for the standardization of permanganate or thiosulphate.[16]

In acid solution, I^- may be oxidized to iodine by means of a wide variety of oxidizing agents, and numerous methods of analysis are based upon this fact. Potassium permanganate in dilute sulphuric acid has been used. Precipitated manganese dioxide and excess of permanganate are removed with oxalic acid and the liberated iodine is titrated with thiosulphate in the presence of carbon tetrachloride. If much Br^- or Cl^- is present, formic acid is added immediately after the addition of oxalic acid.[17] If the iodine produced during the titration is removed by solution in a layer of ethyl acetate, a direct titration with potassium permanganate may be made.[18] In the presence of acetone and sulphuric acid an aqueous solution of an iodide may be titrated with 0·1N-potassium permanganate until a pink colour persists.[19] Iodide in 0·01 – 0·0001N. solution in the presence of a large excess of Cl^- or Br^- may be titrated with permanganate in hydrochloric acid solution. The iodine is finally oxidized to iodine monochloride, and the disappearance of the colour of the iodine from a chloroform extract may be taken as the end-point. If much Cl^- is present, a manganese dioxide emulsion oxidizes all the I^- to iodine monochloride which reacts with thiosulphate as if it were iodine.[20, 21] Iodine liberated from sulphuric acid solution by permanganate may be measured colorimetrically after extraction with carbon tetrachloride.[22] The use of bromoform rather than chloroform helps to hasten the separation of the dispersion produced in the aqueous layer.[23] The liberation and distillation of iodine after treatment with ferric chloride has been proposed.[24] The authors state that the method is accurate, but earlier workers[25] noted a tendency for iodine and steam to react and form hydrogen iodide.

Ceric sulphate has been used to liberate iodine quantitatively from iodides and the end-point may be observed potentiometrically.[26] This reagent can also be used in a titration employing the colour change of *o*-phenanthroline–ferrous sulphate indicator, iodine formed by oxidation of I^- being eliminated by the catalyzed iodination of acetone.[27] Iodide ion in 3N-hydrochloric acid may be oxidized to iodine monochloride by means of a mixture of chloramine-T and sodium perborate added from a burette until the colour of the carbon tetrachloride present is no longer violet.[28] Hydrogen peroxide has been suggested as the oxidant in a solution of known acidity:

$$2I^- + H_2O_2 + 2H^+ \longrightarrow I_2 + 2H_2O$$

The change in acidity is measured by titration with caustic soda after removal of free iodine by means of chloroform.[29] The reaction

$$2HNO_2 + 2I^- + 2H^+ \longrightarrow 2H_2O + I_2 + 2NO,$$

followed by titration of the free iodine with sodium thiosulphate, may be used for the determination of I^-, but to avoid side effects due to the presence of oxygen and nitrogen peroxide, it is advisable first to add urea and then to expel air with carbon dioxide before acidifying the solution.[30] The method has been criticized as giving uncertain results owing to the formation of hypoiodite. In a modified procedure, therefore, the iodine formed on addition of sodium nitrite and sulphuric acid is completely extracted with chloroform and then titrated with standard sodium sulphite solution after addition of sodium bicarbonate.[31]

Numerous refinements both in types of indicator and in operating conditions have been suggested for the direct titration of iodides with silver nitrate. Starch is considered a better protective colloid than gum arabic for holding silver iodide in colloidal suspension, and the following procedure is recommended.[32] To 25 ml. of iodide solution (0·1N) are added 1 drop of 0·1N-potassium iodate and a few drops of 4N-sulphuric acid, followed by starch paste and 5 – 10 ml. of 2N-ammonium carbonate; the solution is then titrated against 0·1N-silver nitrate, shaking vigorously after each addition of silver, the precipitate changing from grey to pure yellow at the end-point. It is claimed that moderate quantities of bromide or chloride may be present without causing interference,[33] although other workers find that some chloride but no bromide may be present during the titration.[34] This technique has been applied to the examination of solutions containing both iodine and potassium iodide.[35] A modification of the procedure is based upon precipitation of silver iodide in nitric acid solution with a measured excess of silver nitrate: the precipitate is filtered off and excess Ag^+ is titrated against potassium iodide solution to a permanent blue-green colour with starch in presence of Ce^{++++} as indicator.[36]

Attempts have been made to provide suitable adsorption indicators which may be used for titrating iodides with silver nitrate, particularly when chlorides or bromides are also present.. The use of Rose Bengal or dimethyldiodofluorescein was originally proposed by Fajans. Using eosin in a solution containing ammonium carbonate, 40 mg. of potassium iodide in the presence of 1 g. of potassium chloride may be titrated with an accuracy of 1%. Eosin cannot be used similarly in the presence of bromide, but in this case starch iodide may be used as indicator.[37] Eosin or Congo red has been recommended also by others.[38] It has been pointed out that when titrations are made using substituted fluoresceins, including Rose Bengal, as indicators, the solution must be violently shaken in a stoppered flask during the addition of silver nitrate; in this way, the error does not exceed 0·3–0·4% in titrating 1 g. of potassium iodide in presence of chloride.[39] Numerous adsorption indicators have been proposed for the titration of iodides argentometrically in slightly alkaline solutions.[40] Among the dyestuffs proposed, which are generally suitable for I^- but not for Br^- or Cl^-, are "Diaminechtbordeaux 6 BS" and "Diaminechtviolett B.B.N." (Cassella),[41] "Diaminbrillantblau G," "Siriusblau F3R," and "Siriusrotviolett B" (I.G.),[42] and also the so-called "multiform" indicator *p*-ethoxychrysoidine which can be used as an acid–base, oxidation–reduction or adsorption indicator.[43] The colour changes with pH of the adsorbates of *p*-ethoxychrysoidine on silver iodide have been discussed.[44]

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Cinchonine bismuth nitrate, which forms a red compound, $C_{19}H_{22}N_2O,HBiI_4$, may also serve as an indicator. The reagent is made by dissolving 2·33 g. of bismuth oxide in 10 ml. of hot concentrated nitric acid and diluting this slightly with water; 2·94 g. of cinchonine are then added, the solution is diluted to 100 ml. and 0·1 g. of urea is added to destroy any nitrous acid. The iodide solution containing a little of the reagent is titrated at pH 4 with silver nitrate until the red colour disappears and only the pale yellow precipitate of silver iodide remains: the results averaged 0·5% low.[45] α-Naphthoflavone has been used as a fluorescent indicator for the titration of iodine in ultra-violet light,[46] and the adsorption indicators proposed for use in the titration of chlorides are often suitable with iodides. Diphenylcarbazide has been used as indicator in the mercurimetric titration of I^-: 12 – 126 mg. of I^- are titrated with mercuric nitrate in 50 – 100 ml. of solution containing 2 ml. of 2N-nitric acid and 7 ml. of 10% aqueous pyridine to remove mercuric iodide.[47]

Iodide may be titrated oxidimetrically with sodium hypochlorite at pH 6·5 – 7·5, the pH being adjusted at intervals during the titration by the addition of sodium dihydrogen phosphate.[48] Ozone has been proposed as a reagent for the oxidation of I^- to periodate. About 0·2 g. of I^- or IO_3^- in 100 ml. of water containing 2 g. of caustic soda are aerated with an ozonized air stream for 30 min; excess of ozone is then removed by blowing with nitrogen and the periodate produced is titrated with thiosulphate or arsenite.[49]

A qualitative test for iodide may be made by treating an aqueous solution with excess of mixed hydrochloric and sulphurous acid solutions when as little as 0·5 mg. of I^- will produce a yellow coloration, possibly due to iodosulphinic acid, which may be extracted by many organic solvents such as amyl alcohol. Chlorides and bromides do not react in this way.[50] A catalytic test depends on the fact that *o*-nitroaniline, its isomers, and other aromatic primary amines, form diphenyl derivatives with monobromobenzene in the presence of iodide and thereby liberate hydrogen bromide. By carrying out the test under strictly controlled conditions with a suitable blank, it is possible to detect, by a comparative colorimetric procedure, the formation of bromide resulting from the presence of 0·05 μg. of I^- in one drop of solution.[51] Filter paper impregnated with 0·1N-silver nitrate solution and dried gives a yellow spot when a drop of solution containing I^- is placed on it: if Br^- and Cl^- are also present they are not precipitated with the iodide but in different zones, and 5 μg. of I^- can thus be detected in the presence of the other halides.[52]

THE ELECTROMETRIC ESTIMATION OF IODIDES

The oxidopotentiometric titration of iodide may be carried out in the presence of Cl^- and Br^-, as a sharp change in potential occurs when all the iodine has been liberated by an energetic oxidizing agent such as potassium dichromate in hydrochloric acid solution:[53,54] other reagents proposed are potassium bromate or iodate; permanganate is less suitable as it may oxidize some iodine to iodate, though later work has shown that under suitable conditions it may be used for this titration,[55] especially in a sulphuric acid solution. Others have confirmed this fact and titrate iodides in a similar manner in presence of carbon tetrachloride to remove the liberated iodine: e.m.f. is plotted against volume of standard solution, and a simple method of using the plot has been outlined.[56] Iodides may also be oxidized with permanganate to iodine monochloride, but the reaction, which may be followed potentiometrically, requires twice as much permanganate as does the oxidation to iodine.[57] A similar technique is effective in the presence of large amounts of chloride and bromide. Two platinum electrodes, one dipping in the solution to be analysed and the other in an aqueous solution of bromine and potassium bromide, are connected electrolytically by the usual potassium chloride bridge. To 50 – 100 ml. of solution to be tested are added 20 – 30 ml. of concentrated hydrochloric acid and 25 ml. of carbon tetrachloride, and the solution is titrated against 0·1N-potassium permanganate.[58] It is said that 0·01N-potassium iodide may be titrated in this way in the presence of four times as much potassium bromide or 100 times as much potassium chloride.[59] The reaction between IO_3^-, I^- and hydrochloric acid, whereby iodine monochloride is formed, may also be followed potentiometrically with a similar electrode system.[60]

Iodides may be titrated in acid solution with iodates and the colour change measured photoelectrically.[61] Iodides may also be titrated conductometrically with lead nitrate, even in the presence of chlorides or bromides, but the end-point is not easy to observe.[62] Iodide can be estimated by a coulometric titration with electrolytically generated bromine using an amperometric end-point, I^- being oxidized to IBr_2^- in 2N-hydrochloric acid and 0·1N-sodium bromide. The indicator current increases to a maximum near the time corresponding to oxidation to iodine, then passes through a minimum near the IBr_2^- equivalent point and finally increases linearly with the concentration of excess Br_3^- produced. The equivalence point is found by extrapolating this final segment to zero current, and 13 μg. I^- can thus be determined within ± 2%.[63]

DETERMINATION OF FREE IODINE AND OF HYPOIODITE

The reaction of iodine with thiosulphate is extensively used for measuring the quantity of iodine present in a solution. In an acid solution, I^- interferes with this titration owing to the reaction of thiosulphate with hydriodic acid, but if potassium thiocyanate instead of iodide is used to dissolve the iodine, the titration may be conducted in the presence of air as the concentration of I^- then becomes so low that the error due to its oxidation is negligible.[64] In titrating acid solutions of iodine it is advisable to add a phosphate or borate buffer solution, and it is also pointed out that, as iodine is lost by evaporation from drops unless precautions are taken, the iodine solution should not fall through more than 1 cm. of air.[65] If an alkaline solution of iodine is titrated with thiosulphate the results are low owing to the formation of hypoiodite; but a large excess of sodium bicarbonate causes an opposite error and the concentration of this salt should not be more than normal.[66] Some workers find that the use of bicarbonate, sodium dihydrogen phosphate or borax in this titration gives variable and low results and suggest the use of calcium carbonate to neutralize any acid present.[67] Others do not entirely endorse these views and find that buffering with bicarbonate, borax or acetate is satisfactory:[68] they also point out that buffering is less important when arsenite solution is used in place of thiosulphate. When thiosulphate is added to iodine in the presence of one or two inert electrodes an end-point is obtained owing to polarization or depolarization and the current becomes zero. This is the so-called "dead-stop end-point".[69, 69a] The oxidation-reduction potentials of the system thiosulphate-tetrathionate obtained by means of iodine and the limits of the tetrathionate region of thiosulphate oxidation have been studied.[70]

An acidimetric determination of iodine has been proposed: an aqueous solution of iodine is treated with silver nitrate and the nitric acid in the filtered reaction mixture is titrated with alkali:[71, 91]

$$5Ag^+ + 3I_2 + 3H_2O \longrightarrow 5AgI + IO_3^- + 6H^+.$$

Sodium acetomercurithymol sulphonate, which is readily obtained in a pure state and has a high molecular weight, reacts with iodine with displacement of the acetomercuric group and the end-point is indicated by starch. It is claimed that the results with this method are more accurate than those obtained with arsenite.[72] Titanous sulphate reacts with iodine in dilute solutions and this may be applied in the following way: to 15 ml. of solution containing about 0·1 g. of iodine, 30 ml. of 0·033N-Ti^{+++} solution are added, a stream of carbon dioxide being passed through the system; after keeping the temperature at 50°C. for 5 min., the solution is cooled and titrated with 0·033N-Fe^{+++} solution in the presence of CNS^- as indicator.[73]

The starch-iodine reaction for the detection and estimation of free iodine has been the subject of much research. It is said that 0·0005 – 0·005 mg. of iodine per ml. of solution may be determined by this reaction.[74] In acid solutions the reaction is inhibited by nitrite, but the presence of thiocyanates prevents the inhibiting action.[75] A study has been made of the numerous factors which change the sensitivity of the reaction.[76] The presence of traces of Hg^{++} or Ag^+ causes the blue colour to disappear and change to yellow.[77] The accuracy of the starch-iodine colorimetric method has been confirmed.[78] The starch solution should first be saturated with iodine to destroy reducing substances; the maximum colour is obtained when 40 mg. of starch is present per mg. of iodine. The dissociation of the starch-iodine compound is the most important source of error in the colorimetric determination of iodine.[79]

Dilute solutions of iodine (<3 mg.) may be shaken with carbon tetrachloride to extract the iodine: the extract is transferred to a flask with 50 ml. of 1% potassium iodide and enough hydrochloric acid to make the solution about 0·001N., and is then titrated with 0·004N-sodium thiosulphate until the carbon tetrachloride is almost colourless, the titration being finished after the addition of starch.[80] When iodine is determined colorimetrically in chloroform solution, low values are obtained in the presence of sodium, magnesium and calcium chlorides, but not with the sulphates.[81] In titrating small quantities of iodine with thiosulphate it is advantageous to work in ultra-violet light with a two layer system obtained by mixing acetic acid, water and chloroform, a suitable fluorescent dyestuff such as purified thioflavin being dissolved in the chloroform. The chloroform does not fluoresce with full brilliance until all the free iodine has disappeared and by using this end-point as little as 25 μg. of iodine can be titrated.[82]

Numerous reagents have been proposed for detecting and determining iodine, but few are reasonably specific. At a dilution in which the starch and chloroform reactions are negative, iodine gives a dark yellow colour with palladous chloride, but bromine behaves similarly.[83] 2:7-Diaminodiphenylene oxide in acetic acid gives a blue coloration with iodine and with most other oxidizing agents.[84] Benzidine acetate behaves similarly and for iodine is sensitive to 1 in 26 × 10^4.[85] In neutral solution (pH 6·5 – 7·5) iodine gives with fluorescein an orange pink di-iodofluorescein proportional to the amount of iodine present: as this compound is non-fluorescent, the loss in fluorescence may be used as a measure of the iodine originally present. It is possible to detect 30 – 150 μg. of iodine colorimetrically, whilst fluorometrically one can detect 2 – 25 μg. or even 1 – 10 μg. under special conditions.[86]

Free iodine may be determined by means of its depolarizing action on an electrode,[87] and the technique has been applied to measuring the iodine liberated from acid potassium iodide by the manganic hydroxide formed from oxygen present in boiler waters.[88] A so-called "iodine meter" based upon similar depolarization effects serves to measure 0·001 μg. of iodine in 1 ml.[89]

Hypoiodous acid in solution may be measured by means of its reaction with phenol. Two portions of the acidified solution are taken and to one phenol is first added; both are then treated with potassium iodide and the liberated iodine is titrated. The difference between these titrations corresponds to the hypoiodous acid present: $HIO + HI \longrightarrow I_2 + H_2O$.[90]

THE DETERMINATION OF IODATE

The classical method for the determination of iodate depends on the reaction $IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$. By viewing the solution to be titrated in a 40 cm. long tube painted black on the sides and illuminated by means of a 150 watt blue bulb, 0·3 μg. of iodine gives a noticeable colour in 15 ml. of solution and so gives a very satisfactory end-point on titration with thiosulphate.[92] Several electrometric methods of determining iodate, some of which depend upon the above reaction, have been proposed.[93,94] If oxidizing acids are titrated potentiometrically in the usual way, there is a danger that some reduction may occur at the same time. This difficulty is overcome by using as anode a thin platinum wire freshly coated with some gold sponge, and connected by a potassium nitrate salt bridge with a calomel electrode. When iodic acid is titrated with caustic soda solution, the end-point is reached with the complete formation of sodium iodate, without any indication of the formation of the acid salts.[95] The reaction

$$IO_3^- + 6H^+ + 6S_2O_3^- \longrightarrow I^- + 3S_4O_6^{--} + 3H_2O$$

may be followed by conductometric titration, using a strong acid as titrant.[96] Iodate may also be titrated electrometrically against silver nitrate in an aqueous methanol solution from which silver iodate is precipitated.[97]

Of the chemical methods proposed for the determination of iodates, the reaction

$$2NaIO_3 + 3N_2H_4 \longrightarrow 2NaI + 6H_2O + 3N_2$$

has been put on a micro scale by measuring the nitrogen evolved in the manometric apparatus of Van Slyke and Neill.[98] The estimation of iodate by precipitation of silver iodate is usually unsatisfactory because of the partial solubility of the precipitate, but a large excess of silver nitrate reduces this solubility sufficiently to allow the method to be used.[99] From a solution of benzidine acetate iodates precipitate an insoluble benzidine bi-hydriodate (solubility about 0·03 g./l.) which can be dried and weighed,[100] though the method is not as precise as titration with thiosulphate after adding acid potassium iodide solution. The reaction with iodide is used with various slight modifications for the determination of iodates in the presence of iodides.[101, 102, 103] By measuring the liberated iodine colorimetrically in chloroform, even 0·008% of potassium iodate in the iodide may be estimated.[104]

Iodate may be detected in the presence of periodate by removing the major part of the latter as potassium periodate and then precipitating IO_3^- with silver nitrate in the presence of dilute nitric acid.[105] For the quantitative separation of iodates and periodates the following procedure is proposed. To 100 ml. of solution containing 10 – 100 mg. of potassium iodate and 10 – 100 mg. of periodate are added 2 ml. of 10% ammonium chloride solution and 2 ml. of concentrated ammonia solution: the mixture is heated to the boiling point, 2 ml. of 10% zinc acetate solution are added, and the zinc periodate is filtered off after the solution has been kept at room temperature for half an hour. The precipitate is dissolved in hydrochloric acid and after addition of potassium iodide, the liberated iodine is titrated: the filtrate from the zinc periodate is treated in the same manner for the determination of iodate.[106]

Sodium thiosulphate, even at low concentrations, reduces iodates in acid solution, but its action of BrO_3^- or ClO_3^- is much less. To 4 – 5 ml. of solution in a test tube are added 2 – 3 drops of starch solution, 5 – 6 drops of dilute sulphuric acid and 1 drop of 0·5% sodium thiosulphate solution: if iodate is present a blue colour is produced and 0·05 mg. of potassium iodate may thus be detected in 10 ml. of solution in presence of 0·1 g. of potassium chlorate or bromate. The method may be varied by covering the mixture with 1 - 2 ml. of 0·5% sodium thiosulphate solution, so that a blue ring appears at the junction of the two solutions if IO_3^- is present. It is possible in this way to detect IO_3^- in presence of ClO_4^-, Cl^-, PO_4^{---}, ClO^-, Fe^{+++}, Cu^{++}, $Cr_2O_7^{--}$, MnO_4^-, etc.[107] The same method may be used with a small amount of chloroform in place of starch solution, so that the liberated iodine acts as its own indicator,[108] while with suitable modifications the procedure can be made quantitative.[109] This may be done by suitably buffering 20 – 30 ml. of solution containing 2 – 3 milliequivalents of iodate, adding 2 g. of potassium biphthalate and 3 g. of potassium iodide: the liberated iodine is titrated after 3 minutes. Chlorate and bromate do not interfere, but may be determined subsequently by adding hydrochloric acid and molybdate catalyst.[110] Iodate may be detected in presence of ClO_3^- and BrO_3^- by means of the coloration resulting from the oxidation of pyrrole in presence of concentrated phosphoric acid.[111]

Several tests are available for detecting the presence of iodate ions, including microchemical crystalline tests with thallous acetate,[112] or nitrate.[113] If a drop of 0·1 M-mercurous nitrate solution is added to a solution containing more than 0·03 mg. of iodate, a white precipitate of mercurous iodate is formed, but it is soluble in excess of the reagent.[114] Iodate ion reacts with pyrogallol in acid solution oxidizing it to red-brown purpurgallin, and ClO_3^-, ClO_4^-, NO_3^- and Fe^{+++} (in presence of oxalic acid) do not interfere: $S_2O_8^{--}$ and BrO_3^- produce different colours, while I^-, CrO_4^{--} and $Cr_2O_7^{--}$ interfere.[115]

THE DETERMINATION OF PERIODATE

Polyalcohols of the type $[CH(OH)]_n(CH_2OH)_2$ (n varying from 0 to 4) reduce (n + 1) HIO_4 to iodic acid with formation of 2 mols..of formaldehyde and n mols. of formic acid. The reaction is quantitative and may be used for the determination of periodic acid in presence of iodic acid.[116] Sodium and potassium periodate resemble periodic acid in oxidizing polyalcohols having two adjacent hydroxyl groupings, but react more slowly. Moreover $K_2H_3IO_6$, like boric acid, appears to form additive compounds with polyalcohols, whereby the oxidation is facilitated.[117] At pH 4·4 – 7 the iodine liberated from potassium iodide in the presence of a mixture of iodate and periodate corresponds to the periodate reduced to iodate, but after the solution is made more acid the iodate also reacts with the iodide.[118,119]

The ion IO_4^- may be reduced to IO_3^- by treatment with sodium arsenite in a solution buffered with sodium bicarbonate containing potassium iodide as catalyst, and the excess of arsenite may then be titrated with iodine in the usual manner.[120] Paraperiodic acid, H_5IO_6, may be determined by heating it with potassium iodide and hydrochloric acid for 15 min. at 60°C. The investigators of this method also record the details of changes involved on heating paraperiodic acid in vacuo to form metaperiodic acid HIO_4 or dimesoperiodic acid $H_4I_2O_9$.[121] The changes in equilibria of the periodic acids in aqueous solution have been followed by observing the extinction coefficients in the ultra-violet region as a function of pH.[122] With periodates in dilute acetic acid solution, zinc acetate gives a white precipitate of $Zn_5(IO_6)_2$ which is readily soluble in dilute mineral acids: when dissolved in nitric acid it gives with silver nitrate a yellow precipitate soluble in excess of nitric acid. Iodic acid does not react in this way.[123]

THE MICRO DETERMINATION OF IODINE

The micro determination of iodine has in the main been carried out by one of three methods, namely (1) by oxidizing iodide to iodate and then adding potassium iodide to an acid solution and titrating the liberated iodine; (2) by liberating free iodine from an iodide and subsequently determining it colorimetrically; or (3) by means of the catalytic effect of iodine ion on the course of several reactions A very extensive literature has been built up dealing with these three methods.

For the first method various specific oxidants have been proposed. One commonly used is potassium permanganate,[124-128] the iodide being oxidized in hot alkaline solution and excess of permanganate destroyed by means of oxalic acid, sodium perborate, or sodium nitrite. The use of chlorine water or alkaline hypochlorites, such as those of sodium or calcium, is equally common:[129-135] excess chlorine may be boiled off after the oxidation is complete and heating will decompose excess of hypochlorite; though some workers prefer to remove hypochlorites with reducing agents such as sodium formate.

The third generally approved oxidizing agent is bromine,[136-150] excess of which may be readily removed by boiling or blowing with air, though some workers prefer to remove it with alkaline formaldehyde or with free formic acid.

Iodine imparts a pink or red colour to many organic liquids and a lengthy series of colorimetric methods has been proposed which are all dependent on this reaction.[151-163] The usual solvents for iodine are xylene, chloroform, carbon disulphide and carbon tetrachloride. The iodine is liberated preferentially by means of nitrite in acid solution but excess of nitrite should be destroyed by means of urea or hydrazoic acid. For very small amounts of iodine, carbon disulphide is considered to be the best solvent.[162] The most widely used colorimetric method which is not based upon solvent extraction makes use of the starch iodide coloration, but other colorimetric tests have been proposed. Thus iodine oxidizes an excess of hydroxylamine in sulphanilic acid to form a diazonium salt which when coupled with α-naphthylamine forms a red dye whereby 1 µg. of iodine may be determined with an accuracy of 2%.[164] Thiofluorescein, which is colourless in acid and blue in alkaline solution, with maximum absorption at 5850A., is oxidized by one atom of iodine per mol. in acid solution and by 2 atoms in an alkaline solution, the product being colourless in either medium. Thus 10^{-8}g.-atom (1·27 µg.) of iodine in 10 ml. viewed through a 1 cm. layer can easily be detected.[165] Another reagent is *o*-tolidine, which gives a blue-green coloration with iodine and will detect 10 µg. in 15 ml. of water: iodate may be reduced to iodide with hydrogen sulphide and the iodine then liberated with hydrogen peroxide.[166]

The catalytic effect of minute amounts of I^- is illustrated by its action on the reaction between arsenious acid and ceric sulphate in sulphuric acid solution.[167-175] Thus the yellow colour of Ce^{++++} in the mixture persists for 2 – 4 days at room temperature, but disappears within a few minutes in the presence of 1 – 2 µg. of I^-. The only other ions which have a comparable effect are osmium and ruthenium, but there are still others which will interfere if present in much larger amounts. (The catalytic effect of osmium is not inhibited by Hg^{++} and in this way osmium and iodine may be distinguished). The quantity of I^- present may be determined by observing with a stop watch the time required for discharge of the yellow colour due to Ce^{++++} Full details have been given for carrying out this test.[167,168] The method has been extensively used to measure a few hundredths of a µg. of I^- in blood serum, tissues, etc. with a standard error of less than 1·5 µg. per 100 ml. Nitric acid may be used in place of Ce^{++++} as the oxidant and alkaline silver nitrate is used to detect the oxidation, a red-brown precipitate of silver arsenate showing the presence of iodine whereas in its absence the precipitate is yellow. This reaction will detect 1 µg. of I^- at a dilution of 1 in 50,000.[176] The slow decolorization of methylene blue in 2 N-hydrochloric acid by means of sulphur dioxide is catalyzed by I^- and quantities up to 4 µg. may be estimated by measuring the degree of fading.[177] Another such method depends on the catalytic formation of lead arsenate: if the test solution is treated with 2 drops of M-sodium arsenite, 7 drops of M-nitric acid 1 drop of M-lead nitrate, and then 1 drop of 6 M-sodium nitrite and allowed to stand for 10 min. with occasional stirring, the formation of a white precipitate indicates the presence of I^- and 0.2 μg. may be detected at a dilution of 1 in 500,000.[178] A general method of measuring catalytic activity has also been described. For iodine, the foregoing reaction between ceric salts and arsenite may be used, the relation between potential change measured by a platinum electrode immersed in the solution and the time being plotted against quantity of iodine.[179]

Much work has been done on the direct and the indirect micro-titration of iodine. Thus iodine may be precipitated with mercuric perchlorate on a silver electrode;[180] or the formation of iodine cyanide may be used,

$$IO_3^- + 2I^- + 3HCN \longrightarrow 3ICN + 3H_2O,$$

a little chloroform being added and the solution titrated in a stoppered bottle from a micro-burette until the solvent layer is colourless.[181] The method of Andrews, whereby I^- is oxidized to iodine monochloride by iodate in presence of much hydrochloric acid, has been adapted to a micro-scale.[182] Micro titrations can serve for estimating free iodine, I^-, IO_3^- and IO_4^- when present together: IO_4^- will liberate iodine on adding boric acid and potassium iodide, whereas IO_3^- reacts only when hydrochloric acid is used in place of the boric acid.[183] In this paper the relevant literature is surveyed critically.

The starch iodide method for determining traces of iodine has always been very popular and many papers have been published on its application. A modified procedure has been described.[184] The criticism that the reaction is unreliable for the determination of iodine[185] has been refuted.[186] Some brands of filter paper contain sufficient starch to be used as indicator papers for the reaction: if a drop of 2 N-acetic acid is placed on such paper and to the centre of the spot is added a drop of the solution to be tested followed by one drop of 0.1 N-potassium nitrite solution, 0·025 μg. of I^- can be detected.[187] To destroy excess of nitrites, hydrazoic acid is often used, as it does not reduce IO_3^- or react with iodine during a titration.[188] A study has been made of the starch iodide coloration using a photoelectric colorimeter.[189]

The determination of traces of iodine in presence of other halides is discussed more fully elsewhere (pages 948–950), but certain broad principles are outlined here. Iodide may be titrated againts mercuric nitrate, prepared by dissolving 0·2775 g. $Hg(NO_3)_2,0{\cdot}5H_2O$ in 1 litre of 2% nitric acid and standardizing against ammonium chloride, sodium nitroprusside being used as indicator.[190] By combining this procedure with Winkler's method of converting the I^- to iodine monobromide, using carbon tetrachloride as indicator, it is possible to determine I^- in the presence of other halides.[191] Microchemically iodide may be detected by mixing a drop of sample solution with a drop of a mixture (1:4) of aniline and sulphuric acid and a little solid potassium dichromate, when the presence of iodide is shown by the formation of crystals of the periodide, $6PhNH_2,3H_2SO_4,HI,I_4$, observable under the microscope; Br^- and Cl^- up to 275 and 600 times the amount of the iodide do not interfere.[192] Traces of I^- can be extracted from large masses of salts by solution in ethanol as described by von Fellenberg, iodates being first reduced to iodides, preferably by hydrazine sulphate or hydrate in hot potassium carbonate solution.[193-4]

Numerous papers have appeared on the micro-determination of iodine in organic matter, in many cases body fluids such as blood or serum. The normal procedures have been employed[195,195a] but a recommended modification condenses by freezing the iodine evolved by combustion in oxygen.[196] Numerous workers prefer to destroy organic matter in a closed system using wet oxidation, followed by distillation of any liberated iodine. Sulphuric acid and hydrogen peroxide have been used as the oxidizing agent,[197] although some prefer the use of chromic acid.[198-200] This oxidation is catalyzed by means of ceric sulphate, and the liberated iodine exists partly in the form of iodate which is subsequently reduced to iodide by means of arsenious acid, which also reduces excess of chromic acid: the iodine may then be distilled into caustic soda or potash. There is said to be a danger that variable amounts of chromate may distil over with the iodine and cause erratic results.[199] A series of comparative micro-determinations of iodine in blood showed no difference between values obtained by dry-ashing and by the wet oxidation method.[201] Several published discussions deal with detailed refinements or give comprehensive references to the literature on the micro-determination of iodine.[202-206]

THE DETERMINATION OF IODINE IN ORGANIC MATTER

The necessity for the determination of iodine in thyroid and its preparations, and the importance of a knowledge of the iodine content of animal tissues, have stimulated the publication of many papers on these subjects. Three main trends are apparent in the determination and the methods described can conveniently be grouped into wet oxidation methods, static combustion methods and dynamic combustion methods.

Numerous techniques have been investigated for carrying out the wet oxidation of organic matter. Thus sulphuric acid-hydrogen peroxide treatment allows iodine to be distilled off without danger of iodate formation because of the presence of sulphurous acid in the digestion mixture.[207] A mixture of sulphuric acid and chromic acid or metal chromate is sometimes used as a catalyst:[208-214] in this case iodine is oxidized to iodate and must be reduced before it is distilled off, preferably with phosphorous acid or arsenious acid. A mixture of nitric, sulphuric and perchloric acids tends to liberate some free iodine while the remainder is converted to iodate. This occurs because perchloric acid reacts differently with iodides according to the temperature, and for this reason the vapour from the digestion must be condensed in an oxidant such as bromine water.[215-217] Alkaline permanganate will also readily oxidize the organic matter and fix the iodine as iodate.[218,219] If perchloric acid with potassium chlorate and disodium hydrogen phosphate is used as the oxidation mixture, all the iodine is oxidized to iodate and numerous subsequent interferences are avoided.[220] The Carius method for iodine is accurate provided that the solution is well diluted when the tube is broken open because silver iodide is appreciably soluble in silver nitrate solution.[221] If 80 - 180 μg. of substance is heated in a Carius tube with 5 ml. of 63% nitric acid and 1g. of mercuric nitrate, the iodine is obtained as iodide which may be oxidized to iodate by the action of bleaching powder.[222] It should be noted that bleaching powder sometimes contains a high percentage of chlorate. Some substances (0.2 - 0.5 g.) may be heated in a Kjeldhal flask with 0.4 g. silver nitrate, 3 g. of potassium persulphate and 10 ml. of concentrated sulphuric acid, the neck of the flask being plugged with glass wool supporting sodium sulphite crystals. After about 90 minutes the mixture is cooled and diluted, the sulphite is destroyed with permanganate, the excess of the latter is reduced with ferrous sulphate, and the excess silver is titrated by the Volhard method.[223] Some substances, such as thyroxine, readily yield their iodine to hydrazine,[224] while others require the action of zinc dust and alcoholic caustic potash.[225]

Early work on the determination of iodine in thyroid by Kendall involved fusion of the organic matter with caustic soda in a nickel crucible, and such a fusion is the basis of numerous methods proposed subsequently.[226-238] Iron oxide and similar interfering bodies are filtered off from the leached melt, this is subsequently treated with bromine to convert iodide to iodate, and after acidification with phosphoric acid, excess bromine is boiled off. Some workers prefer to heat the sample with sodium carbonate, either alone or mixed with potassium carbonate, while borax and potassium nitrate are sometimes added.[239-250] Fusion with a mixture of calcium oxide and soda-lime has been

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recommended,[251] or with calcined manganite which also oxidizes the organic matter.[252] Before titrating the liberated iodine with sodium thiosulphate, it is desirable to cool the solution in ice water to prevent loss by volatilization.[253] The sample (about 0.15 - 0.30 g.) with about 1 ml. of decalin may be ignited in a calorimetric bomb after adding 5 ml. of 2N-caustic potash solution: the iodine is oxidized to potassium iodate which is subsequently reduced to iodide with hydrazine,[254] and may then be distilled off as hydriodic acid.[255] It is recognised that simple ignition of organic matter in presence of an oxidizing agent leads to partial formation of iodate, which will cause subsequent error either if potassium iodide is extracted from the residue with alcohol (in which potassium iodate is insoluble),[256] or if the leached residue is acidified when iodine may be lost owing to the reaction between iodate and iodide.[257-260]

In the dynamic method of combustion the sample is burnt in a stream of air or oxygen, preferably in a silica tube. Some workers prefer to add lime or potassium carbonate to the sample prior to combustion, while a roll of heated platinum gauze helps to complete the reaction. Most of the iodine is evolved as the element which is absorbed in an alkaline solution and then estimated in the usual manner. Some of the iodine may remain, however, in the ash as iodide or iodate[261-273] It is claimed that all the organic iodine is volatilized while inorganically bound iodine remains behind in the ash, whereby a differentiation may be made which is valuable in the analysis of algae and kelp. though this differentiation is only approximately valid.[274]

THE DETERMINATION OF IODINE IN SALT, BRINE AND WATER

The accurate determination of iodine in salt and natural waters has been much studied because of the medical interest in such information. In general, the procedure follows the lines of the micro-determinations of iodine in which iodine is liberated and extracted in an organic solvent for colorimetric measurement, or alternatively iodine is oxidized to iodate which is allowed to react with iodide in acid solution to liberate free iodine. Some workers prefer to extract with alcohol the potassium iodide which has deliberately been added to salt,[275-277] but others find it sufficient to dissolve 100 - 150 g. of the salt in water and to oxidize the iodide to iodate with hypochlorite or bromine water if the titration procedure is to be used, or to liberate iodine with nitrite if a colorimetric technique is preferred.[278-290] Errors may arise owing to the presence of manganic or ferric ions in the oxidized salt solution since these will themselves liberate iodine from acid iodide solutions. A solution of oxalic acid will inhibit the effect of manganic ions, while acidification of the iodate solution with metaphosphoric acid will inhibit the action of ferric ions. Any excess of bromine which may remain even after boiling may be removed by adding a little phenol.[291-293] The use of dioxan has been recommended for the liberation of free iodine from iodides in salt:[294,295] presumably it acts by reason of the peroxides usually present in it.

Iodine in natural waters is similarly determined. It is pointed out that some iodine may exist naturally as iodate or may be oxidized to iodate when nitrite is added to the acid solution for the subsequent colorimetric estimation of the iodine.[296-303] A review of the subject up to 1926 has been published.[304]

THE DETERMINATION OF IODINE IN THE ATMOSPHERE

A method of rapidly scrubbing a current of air through a small quantity of wash liquor, using the apparatus of Cauer, has been described: concentrations of the order of 1 μg. of a gas in 1 cubic metre of air can be measured and as little as 0.75 μg. of iodine was estimated.[305,306] The average concentration of iodine in the atmosphere is 0.3 μg. per cubic metre.[307]

THE DETERMINATION OF IODINE IN SOIL AND MINERALS

The determination of iodine in rocks is usually carried out by submitting the ground material to alkaline decomposition. Some workers, however, report that it is possible to distil off all the iodine by treating the ground rock with concentrated sulphuric acid ar 220 - 230°C., while a stream of air is bubbled through the apparatus.[308] If 5 - 10 g. of soil is heated in a nickel boat in a silica combustion tube in an electric furnace at 850°C. the iodine may be driven off in a current of oxygen and absorbed in 10% caustic soda solution.[309] Other workers prefer to use 25 - 100 g. of soil and to absorb the iodine evolved in potassium carbonate solution. Most soils contain from 3 - 8 parts of iodine per million.[310] A fusion method has been compared with the procedure of Andrew (ignition with potassium carbonate followed by extraction of iodide)[310a] and with the above combustion method for soils; in most cases the fusion method gave slightly higher results. Pulverized soil (5 g.) mixed with caustic potash (15 g.) and a little water in an iron crucible is heated cautiously to decompose silicates and slaked in enough water to form a sludge: a little sulphurous acid is added, the solution is acidified with hydrochloric acid and made alkaline again with potassium carbonate and filtered, the filter being well washed. The filtrate is evaporated until salts begin to crystallize and the iodide removed by extraction with ethanol and finally determined colorimetrically.[311] The combustion method has also been criticized by other workers.[312] It is said that ignition of powdered coal and potassium carbonate results in loss of iodine, but that good results are obtained by heating 30 g. of finely powdered coal with 1.5 g. of potassium carbonate and 400 ml. of 50% alcohol for 8 hr. at 270 - 280°C. in an autoclave. The solution is filtered and evaporated to dryness, the residue being heated gently and extracted with water. The iodine content of coal in Europe varies between 0·85 and 11·17 mg. per kg.[313] It is also said, however, that an optimum ratio of potassium carbonate to coal must be used to get the best results, because excess carbonate causes a slight loss, while too little leads to a considerable loss of iodine.[314]

PHYSICAL METHODS OF ANALYSIS

The high absorption of *X*-rays by iodine has been used to determine iodine in urine, the degree of blackening of a radiographic film being measured photoelectrically.[315] Several miscellaneous electrochemical methods have been proposed for the estimation of iodine. Iodide ion has been measured by the electrocapillary method of D'yachkovski.[316] When a cell with platinum electrodes connected to a galvanometer and filled with 0.1 N-potassium iodide solution is placed between the poles of an electromagnet (field strength 2,000 gauss) a deflection is produced which increases ten times on adding a trace of iodine to the solution. The phenomenon is explained as an increase in the induced current strength due to depolarization of the electrodes by iodine. Similarly when an e.m.f. of a few millivolts is applied to the cell electrodes, the resulting current is increased twentyfold or more in the presence of iodine, and concentrations which give no colour with starch can be detected.[317] A simplified potentiometric method for the micro-determination of iodine has been developed and is stated to give satisfactory results.[318] Iodine may be measured spectrophotometrically in potassium iodide at low concentrations.[319] It has high absorption peaks also in the ultra-violet region, so that toluene, benzene, or potassium iodide solution may be used as solvents: the sensitivity is increased by conversion to IO_3^- and 0.2 μg. of iodine can thus be determined.[320] The starch - iodide coloration may be measured in a spectrophotometer at 575 mμ.[321]

The halides as a group are readily separated from other ions by paper chromatography using butanol saturated with aqueous 1·5 N-ammonia as the eluant.[322]

The use of radioactive iodine, I^{131}, as an indicator in iodine analysis is increasing. After oxidizing any organic matter and then reducing any iodate produced to iodide, iodine is precipitated with palladous chloride, collected on a fritted disk, dried and counted. Recoveries of added radioactive iodine are about 99% and an ultimate sensitivity of 4 microrutherfords is claimed.[323-325] Iodine may also be counted as silver iodide and by β ray counting, concentrations down to 10^{-10} curie/l. have been measured.[326] The iodine content of the thyroid gland is also measured in the living subject by direct β ray counting using a Geiger counter placed opposite the neck.[327-329]

STANDARDIZATION

Hydriodic acid (or an acid solution of an iodide) has been proposed as a standard in oxidimetry because it may be titrated accurately with potassium permanganate using an electrometric end-point.[330]

Iodide ion in hydrochloric acid solution may be titrated accurately to iodine monochloride by means of permanganate, dichromate, iodate or ceric sulphate.[331] A hydrochloric acid solution of iodine monochloride may itself be used for certain volumetric titrations. A stable solution is prepared by dissolving 5·54 g. of potassium iodide and 3·5 g. of potassium iodate in 10 ml. of water and 80 ml. of 6 N-hydrochloric acid: to this 10 ml. of chloroform is added and then, gradually, 0·1 M-potassium iodate until, after shaking, the chloroform layer becomes colourless: the chloroform is then drawn off and the solution diluted to 1 litre.[332,333] Among other uses of such a solution it may serve to estimate arsenious oxide, e.g., by dissolving 0·1 – 0·5 g. of arsenious oxide in caustic soda, acidifying with hydrochloric acid, adding 3 – 4 g. of sodium bicarbonate and 2 – 3 ml. of starch solution and titrating with iodine monochloride:

$$H_2AsO_3^- + ICl + 2HCO_3^- \longrightarrow H_2AsO_4^- + I^- + Cl^- + H_2O + 2CO_2$$

The first small excess of iodine monochloride reacts with sodium iodide and liberates free iodine.[334] $ICl + I^- \longrightarrow I_2 + Cl^-$

The so-called Andrews titrations[334a] have been in use for many years and depend upon the disappearance of the coloration due to iodine in an immiscible solvent such as carbon tetrachloride. When an excess of potassium iodate is present, free iodine is oxidized to iodine monochloride in the presence of sufficient hydrochloric acid. Dyestuffs such as Amaranth, Brilliant Ponceau 5R or Naphthol Blue Black may be used as indicators, instead of immiscible solvents, because the dyestuffs are not destroyed by high concentrations of hydrochloric acid in the presence of a little iodine or iodine monochloride, but are decolorized by a trace of excess iodate. Many substances, such as Sb^{+++}, Fe^{++}, $S_2O_3^{--}$, CNS^-, HSO_3^-, hydrogen peroxide, hydrazine etc., may thus be titrated with an error not exceeding 0·5%.[335]

Standards of purity of some analytical reagents, including iodine, have been proposed;[336] it has been shown that if iodine purified by ordinary methods is compared with iodine of atomic weight purity by titration with sodium thiosulphate solution, agreement is, in general, within 0·02%.[337] Dilute solutions of iodine are stable for months if they are made up in 0·3 M-potassium iodide solution.[338] The application of a statistical technique to the examination of a limited number of precise experimental measurements has been illustrated by a study of the results of sixteen analyses in the determination of the atomic weight of iodine.[339]

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SECTION XXXVIII

THE BIOLOGICAL PROPERTIES OF IODINE

By G.M. DYSON

The biological properties of iodine are evinced in the following circumstances: (1) as a trace element essential to animal and vegetable life; (2) as a bacteriostatic agent or bactericide, and (3), in the form of inorganic iodides, as an expectorant and antisyphilitic remedy.

TOXICITY

Few fatal cases of acute iodine poisoning are recorded; Wintsch[1] records a case where 2 fluid ounces of tincture of iodine (equivalent to 5 g. of iodine) produced fatal results in a man of 70, and Finkelstein[2] has given a survey of such cases. There is experimental evidence[3] to show that colloidal iodine is considerably less toxic by mouth than is an ordinary solution in potassium iodide. Berman and Ivy[4] and others[5,6] have made a detailed study of the acute toxicity of iodine in animals. The fatal dose for man is given as 2–8 g., but recovery after taking 10 g. has been recorded where prompt treatment was available.

The chronic toxicity of iodine in very small doses is related to the subject of the thyroid and will be discussed below. On the other hand the use of iodine or of iodides in therapy can lead to different and allergic reactions. When induced by internal dosage with iodides, the condition of 'iodism' is set up,[7] where headache, catarrh and an 'iodine rash' are observed. This condition appears to be different from the allergic dermatitis set up by the continued application of iodine solutions to the skin.[8,9]

Iodates are several times as toxic as iodides;[10] moreover they share with bromates the ability to cause retinal degeneration,[11,12] and disturbance of the glycæmic function.[13] These observations are of importance in relation to the widespread use of bromate, and the suggested use of iodate, in maintaining loaf volume in baking,[14,15] and the patented applications of iodate[16] as a preservative in canned foods,[17] cheese,[18,19] fish[20] and milk.[21]

BACTERIOSTATIC AND BACTERICIDAL ACTION

Iodine has been used in various forms for many years as a first-aid local application in cuts and abrasions and as routine surgical procedure in the sterilization of operation sites, and despite the advent of innumerable antiseptics of apparently higher laboratory activity the use of iodine for these purposes has persisted; there are some who assert that it is still the best antiseptic where (as in pre-operative preparation) the maintenance of a sterile area after one application is the most important factor.[22,23] Iodine is of particular value in disinfection of dermatophytes;[24] its fungistatic action is apparently independent of pH,[25] Gershenfeld[26] showed that, using *E.typhosa* and *Staph. aureus* as test organisms, iodine showed a marked superiority to organo-mercurial antiseptics; this has been many times confirmed.[27-36]

The specific action of iodine solutions on a variety of organisms has been widely investigated;[37] against *Mycobacterium tuberculosis*,[38,39] *Trichomonas*[40,41] *Clostridium welchii* and *C. tetani*[42] and other spore-bearing organisms e.g.

B. vulgatus, *B. subtilis* and *B. cereus*,[43] together with *Leptospira icterohaemorrhagiae*[44] and members of the typhoid group[45] *E. typhi*, *paratyphosus B* and *C*, and *E. coli*.[46] iodine shows a powerful bactericidal activity; with yeasts[47-49] minute traces act as stimulants to reproduction though larger amounts inhibit the growth. Certain parasites, e.g. *Eimeria tenella*[50] are inactivated by iodine, which also plays an important part in the fixation of *Trichinella*[51] in muscle. Iodine is also capable of inactivating certain viruses.[52-56] The use of iodine as an emergency sterilizing agent for drinking water[57,58] has been suggested. The mode of action of iodine as an antiseptic has been correlated with its demonstrable adsorption by bacteria.[59,60] The activity of iodine is increased in the presence of inorganic oxidation-reduction systems[61] such as $MnSO_4/Fe_2(SO_4)_3$. Iodine is an effective fungistatic agent in ringworm or athlete's foot,[62] in the control of smut on oats,[63,64] and in potato ring-rot and scab.[65]

METABOLISM AND THYROID FUNCTION

The relation of iodine and its organic derivatives to thyroid function has been the subject of many thousands of communications in the literature. It is not within the terms of reference of this volume to discuss all this literature, but a number of the chemical aspects of this topic are summarized below. The ancient Greeks treated goitre with the iodine-rich ash of sponges, and in 1820 (only a few years after the isolation of the element) Coindet initiated the treatment of goitre with iodine preparations. Soon afterwards Chatin (1850–70) proved that goitre is associated with iodine deficiency and in the period 1882-1891 Horsley and Murray confirmed the relation between goitre and the thyroid gland. Baumann in 1895 established the high iodine content of thyroid from which in 1915 Kendall isolated thyroxine, the structure and synthesis of which was elucidated by Harington a few years later.

The main facts concerning iodine as a trace element in human nutrition are as follows. The presence of iodine in the alimentary intake of mammals is essential; complete absence or deficiency leads to goitre - an enlargement of the thyroid - whereby an attempt is made by the organism to secure more iodine by increasing the volume of blood traversing the gland. The addition of iodine to the diet will cure early cases of goitre, but severe and old-standing goitres do not regress and must be treated surgically. The minimum amount of iodine for a normal individual is 80–100 γ per day;[66] of this quantity about 30 γ is excreted in the urine, 10 γ via the lungs and up to 50 γ through the skin.[67] The normal iodine content of blood is 12 γ per 100 ml.[68,69] It should be emphasized that whilst simple (endemic) goitre follows a deficiency of iodine intake, other goitres (toxic adenomatous goitre and exophthalmic goitre) are the result of thyroid derangement, as also is cretinism; these, not directly related to iodine deficiency, will not be discussed further.

The recognition of the interrelation of iodine and thyroid activity led to much research (*a*) on the normal intake of iodine in food and drink (*b*) on the relation between endemic goitre and water supplies and (*c*) on the best way of combating iodine deficiency. A by-product of this work was a study of the analytical methods available for the determination of minute quantities of iodine in biological materials.[70-74]

The occurrence of iodine in small amounts in foodstuffs has already been mentioned (see page 817) and it has been shown that the iodine content of vegetable foods is a function of the iodine content of the soil and water used; irrigation with sea-water or water from estuaries where some sea-water is present results in a high iodine content of vegetables.[75] The relation between vegetable iodine and goitre is illustrated by the fact that 19 per 1000 of drafted men from eastern Minnesota but only 7·5 per 1000 from western Minnesota were goitrous. The average iodine content of potatoes[76] in the east was 85 γ/kg. and in the west was 226 γ/kg. This variation in the iodine content of vegetables is common and it is possible, therefore, only to indicate which vegetables have normally a high iodine content. Those which are consistently high are asparagus,95 γ (per 100 g. of dried material)[75] radish, lettuce,[78] carrots, turnip greens, beet-tops 50–90 γ; spinach 100 γ;[77] onion 80 γ; cabbage 150 γ; spinach up to 500 γ;[80] and cucumber 100 γ. All workers report especially high values for asparagus, but these are probably due to the custom of dressing asparagus beds heavily with agricultural salt, which is rich in iodine. It has been shown that the iodine content of cabbage is related to that of the soil in which it is grown.[79] The same relationship holds for milk.[81] A very high iodine content has been reported for watercress – up to 45 mg./100 g.[82] Sea-food is extremely rich in iodine,[83,84,86-88] and varies very little from area to area; oysters[84,92] show up to 1150 γ per 100 g., crab-meat has[89-91] the highest iodine content of any normal food (2000 γ per 100 g.) with the possible exception of shrimp (2300 γ). Salmon is also rich in iodine.[93-95]

It follows that the normal human intake of iodine will depend on the area where vegetables are grown and on the accessibility of sea-food. There are many areas where the iodine intake is below that necessary for normal life: British Columbia,[96] England,[97] Finland,[98] Ireland,[99] New Zealand,[100,102] Hungary,[102,103] Norway,[104] Switzerland,[105] U.S.A.,[106-109] and U.S.S.R.[110,111] In Java and Japan, countries with a large seaboard where seaweed is a constant part of the diet, there is no goitre.[112] On the other hand an abnormally high intake of calcium is apparently able to neutralize some of the iodine as an effective trace-element. Thus a water with low calcium and a given, but marginal, iodine content may not lead to goitre, whereas the same water with higher calcium may become goitrogenic.

Thus, the question has arisen of measures to avoid the goitrous sequel of iodine deficiency; these have consisted principally in adding iodide to the water supply[113-115] and using an iodized salt or sea-salt as a condiment. The use of supplementary iodine in animal husbandry is also a valuable aid to animal health and productivity. Egg-yield and viability in poultry is increased;[116-127] in sheep iodine must be used with discretion,[128-138] applying only just enough to eliminate enlarged thyroid; with pigs the average daily growth is increased.[139,140] In cattle-breeding, the number of successful 'takes' is increased by a small supplementary quantity of iodine, and claims have been made for a higher milk yield in cows, but this does not seem yet to have been fully substantiated.[141-150]

The place of iodine in plant economy is uncertain; in normal plants it is not clear whether traces of iodine are essential to development,[151-157] although in sea-weed economy iodine plays an important part.

Much of the research on the fate of iodine in animal and plant systems has been aided by the use of the radioactive iodine isotope ^{131}I (see page 1056) and a considerable literature has grown up around the technique of the use of this substance both as its simple inorganic derivatives and as its organic derivatives (e.g. di-iodotyrosine and thyroxine); an excellent introduction to this literature is given by the papers of Chaikoff and his coworkers.[158-168]

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CHAPTER V

RADIOCHEMISTRY

SECTION XXXIX

TABLE OF HALOGEN ISOTOPES

The following table of data on the radioactive and stable isotopes of the halogen elements has been prepared directly from the 'Table of Isotopes' by J.M. Hollander, I. Perlman and G.T. Seaborg dated December, 1952,[1] with the kind permission of the authors.

This introduction, based on that of the original Table, has been amplified where necessary by Mr. J. L. Putman, of the Isotope Division, Atomic Energy Research Establishment, Harwell, to render it more readily intelligible to readers whose interests are primarily chemical.

A description of the entries in various columns is given below, followed by a table listing some frequently used abbreviations.

ISOTOPE

The first and last columns list the atomic numbers, chemical symbols and mass numbers of the nuclear species. Separate entries have been made for each nuclear state whose half-life has been experimentally determined. Metastable excited states are denoted by the superscript 'm' following the mass number.

CLASS AND IDENTIFICATION

The degree of certainty of each isotopic assignment is indicated by a letter, according to the following code:

A. Element and mass number certain
B. Element certain and mass number probable
D. Element certain but mass number not well established
E. Element probable and mass number not well established or unknown (mass number not listed means that it is unknown).

Data which have been shown to be in error have in general been eliminated from the Table.

The means by which the mass assignments were made are next tabulated. In general, several references are given here in italics, the first of which denotes the probable discoverer of the isotope. Following this, references are given to the paper or papers which contributed most significantly towards giving the isotope its best or present rating. Some indication of the experimental methods used in making the various assignments may be had from the following symbolism:

chem	Chemical separations, establishing uniquely the chemical identity (atomic number) of the isotope
genet	Proven genetic relationships (by chemical or other means) with other isotopes whose mass assignments are presumably known.

excit	Loosely refers to energetic considerations which have aided in making the mass assignment. Some of these might be: (1) Excitation or yield experiments to establish the nuclear reaction which produces the isotope (2) Bombardments with low energy particles, in which possible products are few (3) Mass calculations, or other estimates or measurements of Q values (4) In a few cases, use of fission yield data in making assignments
cross bomb	Studies of yields of the isotope in several different types of bombardments, in which the target elements as well as the projectiles have been varied
n-capt	Cases where bombardments with slow neutrons (n-γ reactions) have provided key evidence in the mass assignments
sep isotopes	The use of target elements enriched or depleted in a certain isotope
decay charac	Identification of expected or predicted decay characteristics

PERCENTAGE ABUNDANCE

The relative isotopic abundances for the elements are given in accordance with the 'best values' listed in the report by K.T. Bainbridge and A.O. Nier.[2] For some of the light elements reference is made also to papers which discuss source variations in isotopic abundance.

TYPE OF DECAY

The observed modes of decay have been listed for all radioactive nuclei. In cases of branched decay between two or more modes, the branching ratios are listed wherever they are known. Symbols used are:

β^-	Negative beta particle (negatron) emission
β^+	Positive beta particle (positron) emission
α	Alpha particle emission
EC	Orbital electron capture. It may be assumed that X-rays have been observed or actually identified in virtually all cases of orbital electron capture listed. If the ratio of L electron capture to K electron capture has been determined, it is given here as L/K
IT	Isomeric transition (transition from upper to lower isomeric state of same nucleus)
n	Neutron emission

When experimenters have searched for and failed to find a particular mode of decay, this is indicated, for example, as 'no β^+'. Experimental upper limits are frequently given, but no theoretically predicted limits have been quoted.

Among the heavy alpha-emitting isotopes, calculations by means of closed radioactive decay cycles have shown that many of these isotopes are thermodynamically stable against β^-, β^+, or EC decay. This has been indicated by the term 'β-stable', followed by an abbreviation for the principle of conservation of energy, which is used in the calculations.

HALF-LIFE

Half-life values are listed without qualification where the determination has been a direct measurement of decay rate. In other cases, the experimental methods have been described with the aid of the following symbols.

sp act	Determination by weighing a long lived isotope of known purity
yield	Estimation of half-life from the amount of activity resulting from a nuclear reaction whose cross section (or yield) is known or estimated
genet	Measurement of the half-life of a parent activity by determining the yield of a daughter activity as a function of time, where periodic chemical separations of daughter from parent have been performed.

An attempt has been made to list the best value or values first. However, in a few cases where many values of comparable precision have been reported and no choice seemed obvious, an average value for the half-life has been listed; this is explicitly stated, and references are given to all the papers whose values contributed to that average.

PARTICLE ENERGIES

The particle energies are followed by other relevant information pertaining to the decay scheme and by a description of the experimental methods used in obtaining the data. In cases of complex alpha structure or several partial beta spectra, the relative abundances of the various groups within that mode of decay are given in parentheses.

Beta particle energies correspond to the upper limits of the spectra.

Alpha particle energies have been quoted only where the investigator has actually measured them.

Conversion electron energies are listed only when it is not known in which shell internal conversion takes place or when no attempt was made by the experimenter to relate the electrons with observed or unobserved gamma rays; in all other cases, entries are made in the column for gamma transitions.

Experimental methods are described as follows:

abs	*Absorption* of the radiation. The absorption of β^- and β^+ particles in increasing thicknesses of material is at first nearly exponential, but a maximum range is eventually reached. Both the initial absorption and the maximum range are measures of the original energy of the particles.
coinc abs	β-and γ-*counters with absorbers* can be *coupled to a coincidence equipment*, which registers only when a count is obtained simultaneously in both counters. This method is sometimes used for the selection of particles or gamma-rays in complex breakdown schemes.
spect	In a *beta-spectrometer*, the energy of the radiations is found from their deflection in a magnetic field.
coinc spect	Denotes coincidence methods (see coinc abs) used in conjunction with a beta-spectrometer.
scint spect	In the scintillation counter, radiations falling on a crystal, or other phosphor, produce scintillations of light which are converted to electrical impulses with a photomultiplier. Using certain phosphors, the amplitude of the impulses is proportional to the energy given up by the radiations. The arrangement can therefore be used as a *scintillation spectrometer* to determine energies of the radiations.
cl ch	By the use of a Wilson cloud chamber the tracks of particles are made visible when vapour is condensed

	on the charged ions they leave behind. The cloud chamber is used with magnetic fields to determine the deflection and hence the energy of β^- and β^+ particles.
ion ch	The ionization per cm. of path, as well as the total ionization, produced by a beta-particle depends on its energy. In the pulse *ion chamber* and in the *proportional counter,* electrical pulses are produced whose amplitude is proportional to the ionization in the chamber. These can be used to deduce the energy of the radiations.

GAMMA TRANSITIONS

Gamma transitions are described by the following information, in so far as reliable data permit:

Energy of the gamma quantum. When internal conversion electrons form the basis for the energy determination, the energy listed in this column is always that of the corresponding gamma ray transition.

Abundance of gamma rays. This may be given as the number of unconverted gamma rays emitted per 100 disintegrations. Where an absolute abundance has not been determined, often the relative unconverted gamma ray abundances have been measured. These are tabulated, for example as $\gamma_1/\gamma_2/\gamma_3 \approx 2/1/5$.

Internal conversion coefficients. These are given for each gamma transition as the ratio of the number of conversion electrons emitted to the number of unconverted gamma quanta emitted, and are expressed as e/γ. Where conversion coefficients for individual electron shells have been determined, they are denoted as e_K/γ, e_L/γ etc.

Conversion coefficient ratios. Where the ratios of internal conversion coefficients in several electron shells have been measured, they are listed as K/L, L/M, K/L+M, K/L/M, $L_I/L_{II}/L_{III}$, etc.

When an author states that gamma radiation is present, but reports no energy determination, this is indicated by the symbol 'γ'. Conversely, when attempts to find gamma radiation have failed, this has been indicated by 'no γ'.

X-Rays have been mentioned only when they are the prominent radiation observed in measuring an activity, or when the observation and identification of *X*-rays has been crucial in the characterization of an isotope.

The symbols used to describe the methods employed for the determination of gamma ray energies or for the elucidation of decay schemes are as follows:

abs	*Absorption* of the radiations. The number of gamma-ray quanta decreases exponentially with the thickness of the absorber, and the rate of decrease is a measure of their energy.
abs sec	*Absorption* of the *secondary electrons* produced by the photo-electric effect of γ-rays on matter. The energy of such photo-electrons is equal to that of the original γ-rays minus the ionization energy needed to eject the photo-electrons from atoms of the absorber.
abs conv	*Absorption of internal conversion electrons*
coinc abs	Coindicence studies using absorption techniques (see PARTICLE ENERGIES)
spect	Use of the magnetic beta-spectrometer (see PARTICLE ENERGIES) to measure the energy of *secondary electrons* produced by gamma-rays in matter.
spect conv	Use of the beta-spectrometer (see PARTICLE ENERGIES) to measure the energy of *internal conversion electrons*.

Coinc spect	Use of the *beta-spectrometer* in connection with other counters in a coincidence arrangement (see PARTICLE ENERGIES, coinc abs). Coincidences with other gamma-rays, with conversion electrons from other gamma-rays, with beta-particles etc. are used to identify the particular gamma-ray being measured and to determine its relation to the decay scheme of the radioisotope.
scint spect	(See PARTICLE ENERGIES). The energy of the gamma-rays is generally deduced from the pulses produced when gamma-rays are completely absorbed in the phosphor; *i.e.* from the energy of photo-electrons produced in the phosphor. It can also be deduced from the maximum energy of recoil electrons produced by the Compton recoil process in the phosphor.
cryst spect	Estimation of wave-length and therefore energy from the *diffraction* of gamma-rays in a *crystal.* This is a standard method by which the wave-lengths of *X*-rays are determined in terms of the spacing between planes in the crystal structure. It is generally applied only to low energy gamma-rays, whose wave-lengths are not too short compared with the spacing of crystal planes.
cl ch recoil	Measurement of the energy of *Compton recoil electrons or photo-electrons* by means of a Wilson *cloud chamber* (see PARTICLE ENERGIES, cl ch).
Be-γ-n, and D-γ-n:	Measurement of gamma-ray energy from *secondary nuclear reactions* produced by the gamma-rays. Be-γ-n represents the bombardment of a beryllium nucleus with a gamma-ray and the consequent emission of a neutron. The energy of the gamma-ray is deduced from the measured energy of the neutron. D-γ-n represents a similar reaction using deuterium.

DISINTEGRATION ENERGY AND SCHEME

The disintegration energy (Q) of a nuclear decay process is defined as the mass difference of the initial and final atoms, transformed into units of energy (1 atomic mass unit = 931 MeV.). It is equal to the sum of the kinetic energies of the particles emitted, plus the energies of any gamma-rays which may follow them, plus the energy of recoil of the nucleus. Note that when positrons are emitted the energy (1·02 MeV.) of the annihilation radiations must be included. Where Q values have been estimated or calculated by the authors of this compilation, the special reference 'HPS' is used; otherwise, reference is made to the paper from which the quoted value is taken. In most instances Q values have been obtained from decay data; where this is not the case, the method is indicated.

Energy level diagrams have been drawn in many cases; these are not necessarily complete representations of the data, but sometimes include only those features which are reasonably well established and unambiguous. β^- particles are represented by lines sloping downwards from left to right. β^+ particles and electron capture processes are shown as lines sloping downwards from right to left. Gamma-rays are shown as vertical lines. Thus vertical displacement represents loss of energy, and horizontal displacement represents change of atomic number. Where alternative modes of decay exist, all are shown, and the percentage of disintegrations proceeding by each mode is indicated. Heights of the various energy levels above the ground state are indicated at the side of the drawing. Similarly, the total angular momentum (spin) and parity of the states have been included in some cases, where these quantum numbers could be inferred with some confidence from determinations of conversion coefficients, K/L ratios, ft values, etc. We have relied heavily on the interpretation of decay data by Goldhaber and Hill.[3]

Refs. p. 968

For β^-, β^+, α, or EC decay, the percentage figures given in the decay drawings total 100% for *each* mode of decay, thus expressing only the relative abundances of various groups within that mode of decay. (Branching ratios between the several modes of decay are found in the 'Type of Decay' column). In the case of gamma radiation, however, the percentages given refer to the fraction of the total disintegrations of that isotope which give rise to the gamma ray and its conversion electron. This has been done because of the difficulty of assigning a gamma ray to a particular mode of decay.

Measured values for the mechanical or spin moment, I, of stable or long lived isotopes have also been given in this column. Except as supplemented by more recent data, the values given here are taken from the compilation by Mack.[4]

METHOD OF PRODUCTION AND GENETIC RELATIONSHIPS

The ninth column of the table gives the nuclear features (target element, projectile, and outgoing particle, in order) by which the radioactive isotopes are formed. The corresponding references are listed: (p-proton, n-neutron, α-alpha particle, d-deuteron, t-triton, γ-gamma ray or X-ray, e-electron, π-pi meson, C-carbon ion). In cases in which the target material is not the naturally occurring element, but one enriched or depleted in a particular isotope, the isotope responsible for the reaction is indicated. No means for identifying the source or energy of the projectile is given.

In nuclear reactions with high energy projectiles, multiple particle ejection is common. Rather than attempting to state definitely the path by which the product nucleus was reached, these spallation reactions are briefly represented by the abbreviation 'spall', followed by the symbol of the target element. High energy fission reactions are similarly represented by the words 'spall-fission', and thermal or low energy neutron fission simply by 'fission'.

The criterion for listing genetic relationships has been with few exceptions that these relationships be demonstrated experimentally; for example, by chemical 'milking' of daughter activities, analysis of growth decay curves, or, in the case of short lived isomers, by delayed coincidence experiments. The listing of these parent-daughter relationships gives some warning to the reader as to what he may expect in the way of radiation from a given isotope, since a sufficiently short lived daughter's radiation will usually be observed with that of the parent.

A few further abbreviations are listed below:

[ ]	Properties listed in brackets have not been observed directly, but have been inferred from other experimental data.
est calc	Estimated or calculated from theoretical or empirical considerations.
lim	Experimental upper limit.
emuls	Photographic emulsion.

References

1 Hollander, J. M., Perlman, I. & Seaborg, G. T., *Document No. UCRL*, 1928. *U.S. Atomic Energy Commission,*

2 Bainbridge, K. T. & Nier, A. O., *Natl. Res. Council Nuclear Energy Series, Preliminary Report No. 9.*, Dec. 1950.

3 Goldhaber, M. & Hill, R. D., *Rev. Mod. Phys.*, 1952,24,179. (47,2046)

4 Mack, J. E., *Rev. Mod. Phys.*, 1950,22,64. (44,5205)

TABLE OF
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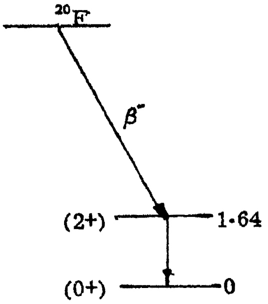
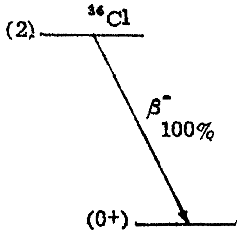
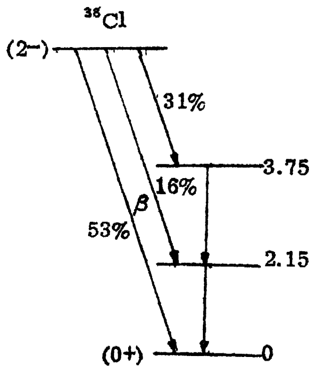
Isotope	Class and identification	Percent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles	
$^{17}_{9}F$	A cross bomb[1,2]; chem, excit[3,4,5]		β^{+} [3]	70 s[3,6]; 60 s[7]; 66 s[8], 72 s[9]; 74 s[5]	1·72 spect[6]; 1·7 abs[8]; 2·1 cl ch[10]	
^{18}F	A chem[17]; chem, sep isotopes, excit[5]		β^{+} [17]	112 m[17,9,18]; 115 m[19]; 107 m[5]	0·649 spect[20]; 0·635 spect[18]; others[21,22,23,24]	
^{19}F		100[37]				
^{20}F	A excit[39,15,40]		β^{-} [39]	10·7 s[41]; 12 s[39]	5·41, no ~7 β^{-} (lim 1%) spect[42]; 5·33 (97%), 6·7 (3%) spect[43]; 5·0 spect, abs[44]; others[45]	
$^{33}_{17}Cl$	A excit[50]; excit[51]		β^{+} [51]	2·8 s[50,52]; 2·4 s[51]; 1·8 s[53]	4·13 cl ch[51]; 4·4 scint spect[53]	

TABLE OF HALOGEN ISOTOPES

	Radiation energy, MeV. γ-Transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
	no $\gamma^{11,12}$	Q^{+}_{β} 2·74^{13}	N-α-n^{1,2,14}; O-d-n^{3,15,6}; O-p-γ^{5}; F-γ-2n^{16,9,7}	$^{17}_{9}$F
	no $\gamma^{25,18}$	Q^{+}_{β}1·67^{20}	O-α-pn^{26}; ^{18}O-p-n^{5}; O-d-n^{21,27,28}; O-^{3}He-p^{29}; O-t-n^{23}; F-n-2n^{30}; F-d-t^{22,31}; F-γ-n^{19,16,9,32,7}; F-p-pn^{20}; Ne-d-α^{17}; Na-γ-αn^{16,33}; spall Al^{34,35}, Cu^{36,35}, Cl, Ag, Au^{35}	^{18}F
		^{19}F, I = ½^{38}		^{19}F
	1·631, no 2·5 γ (lim 0·2%) spect, Be-γ-n reaction^{42}; 1·64, no 2·5 γ spect, γ-γ coinc^{43}; 1·64, 2·5 (weak) spect, abs sec^{44}; 2·2 cl ch recoil^{45}; γ (coinc with 5·0β^{-}) β-γ coinc^{46,44}	Q^{-}_{β} 7·04^{42}  Ref^{42}	F-d-p^{39,15,41,44,47,42}; F-n-$\gamma^{40,48,49}$; Na-n-α^{40}	^{20}F
			S-d-n^{50,52}; S-p-n^{51}; Cl-γ-2n^{53}	$^{33}_{17}$Cl

Isotope	Class and identification	Per cent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles	
^{34}Cl	A chem, excit[54]; chem, excit[55]		β^+ [54,56]	33·2 m[57]; 33·0 m[9], 33 m[55,56]	4·5 (46%), 2·6 (28%), 1·3 (26%) spect[20]; 5·1 (~80%), 2·4 (~20%) cl ch[58]	
^{35}Cl		75·4[65]				
^{36}Cl	A chem, n-capt[66]		β^- [66]; no β^+ (lim 0·01%)[67]; (lim 0·03%)[68]	4·4×10^5 y sp act[67]; 3·6×10^5 y sp act[69]; 2·0×10^5 y yield[69]; 2×10^6 y yield[70]; ~10^6 y yield[71]	0·714 spect[72]; 0·66 abs[71]; 0·64 abs[66]; others[73,74]	
^{37}Cl		24·6[65]				
^{38}Cl	A chem, n-capt[76]; chem, sep isotopes[77]		β^- [10]	37·29 m[78]; 37·5 m[79,80]; 37·0 m[81,82]; 38·5 m[83]	4·81 (53%), 2·77 (16%) 1·11 (31%) spect[84]; 5·0, 2·8, 1·1 spect[85]; spect, coinc abs[86], 5·2 (53%), 2·70 (11%), 1·19 (36%) spect[83]	

Radiation energy, MeV. γ- Transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
3·22, 2·10, 1·16 scint spect[59]; 3·3, 2·1, 0·145 spect, spect conv[20]; 3·4 cl ch recoil[58]	Q^{+}_{β} 5·6[20]	Al-^{12}C-αn[60]; P-α-n[54,14,56]; S-d-n[55,58]; S-α, pn[61]; S-p-n[20]; S-t-n[23]; Cl-n-2n[30]; Cl-p-pn[20]; Cl-γ-n[62,19,9,57,32]; spall Fe[63],Cu[64]	$^{34}_{17}$Cl
	^{35}Cl, I = $\frac{3}{2}$[38]		^{35}Cl
no γ[67]	Q^{-}_{β} 0·714[73,72] ^{36}Cl, I = 2[38,75]  Ref[67]	Cl-n-γ[66,71,48]; Cl-d-p[66]	^{36}Cl
	^{37}Cl, I = $\frac{3}{2}$[38]		^{37}Cl
γ_1 2·15, γ_2 1·60 ($\gamma_1/\gamma_2 \approx$ 1·3) spect[83]; γ_1 2·19, γ_2 1·64 (γ_1 coinc with γ_2) spect, coinc[87]; 2·15, 1·65 spect[80]; no 3·75 γ (lim 0·03%) Be-γ-n reaction[88]	Q^{-}_{β} 4·81[13]  ^{38}Cl (2−) 31% 3.75 16% β 53% 2.15 (0+) 0 Refs[84,83]	Cl-d-p[10,81]; Cl-n-γ[76,77,89,48]; ^{37}Cl-n-γ[77]; K-n-α[79]; spall Fe[63], Co[90], Cu[91,64]; spall-fission Cu[92]	^{38}Cl

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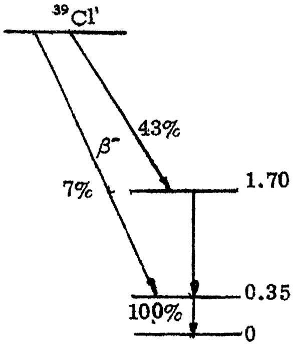
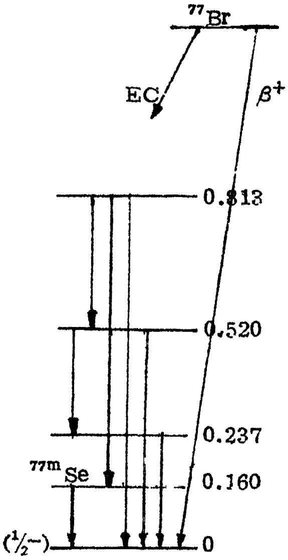
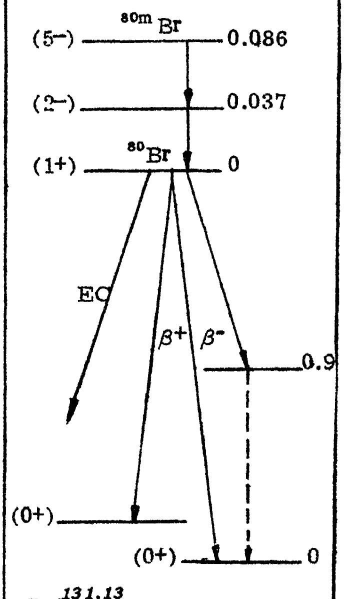
Isotope	Class and identification	Per cent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles	
$^{39}_{17}$Cl	A chem[93], chem, excit[94]		β^-[94]	55·5 m[94]; $\sim$1 h[93,95]	1·65(93%), 2·96(7%) abs[96]	
$^{74}_{35}$Br	D chem[97]		β^+, EC[97]	$\sim$35 m[97]		
^{75}Br	B chem, cross bomb, sep isotopes[98]		β^+, EC[98]	1·6 h[97], 1·7 h[98]	1·70(46%), 0·8(20%), 0·6(15%), 0·3(19%) spect[99] $\sim$1·8 abs[97]	
^{76}Br	A chem[100]; chem, excit[97]; chem, sep isotopes[99]		β^+[100]	17·2 h[99]; 16·5 h[97]; 15·7 h[100]	3·57(46%), 1·7(10%), 1·1(11%), 0·8(14%), 0·6(19%) spect[99]; 3·5 spect[97]	

	Radiation energy, MeV. γ-Transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
	1·35, 0·35 (coinc with 1·65 β^-) coinc abs sec[96]	Q^-_β 3·3[96]  $^{39}Cl'$ 43% β^- 7% 1.70 0.35 100% 0 Ref[96]	A-γ-p[94,96]; spall Fe[63], Co[90], Cu[93,64], As[95]	$^{39}_{17}Cl$
			Cu-C-3n[97]	$^{74}_{35}Br$
	~0·6 abs[99]		Cu-C-2n[97], ^{74}Se-d-n[98]; ^{74}Se-p-γ[98,99]	^{75}Br
	1·2, 0·96, 0·75, 0·68, 0·42, 0·37, 0·33, 0·25 spect, spect conv[99]; ~2 abs[100]	Q^-_β 4·6[99]	As-α-3n[100,97]; ^{76}Se-p-n[99]	^{76}Br

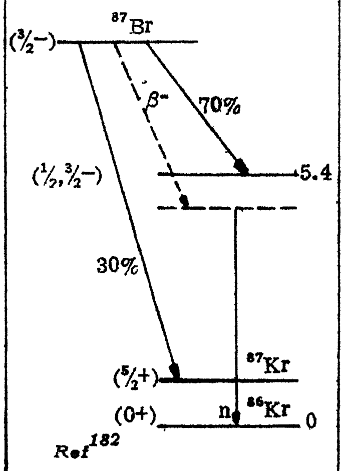
Isotope	Class and identification	Per cent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles	
$^{77}_{35}$Br	A chem, sep isotopes[98]		EC 95%, β^+ 5%[98]	57 h[100,97], 58 h[98]	0.336 spect[101], 0.36 spect[100], abs, spect[98]	
^{78}Br	A chem, excit[103]		β^+[103]	6.4 m[103], 6.5 m[97]	2.4 abs[104] calc from 103 2.3 abs[103]	
^{79}Br		50.52[109]				
^{80m}Br	A chem. n-capt[76], chem, excit, cross bomb[103]		IT[110]	4.58 h[111]; 4.5 h[103]; 4.4 h[106]		

	Radiation energy, MeV. γ-Transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
	γ_1 0·160, γ_2 0·237, γ_3 0·284, γ_4 0·298, γ_5 0·520, γ_6 0·641, γ_7 0·813 ($\gamma_1/\gamma_2/\gamma_3/\gamma_4/\gamma_5/\gamma_6/\gamma_7$ = 0·6/20/0·2/0·2/100/8·6/25) spect, spect conv[101]; 0·160, 0·234, 0·299, 0·521 spect conv, x-γ coinc[99]	See[154,131]  ^{77}Br EC β^+ 0.813 0.520 0.237 ^{77m}Se 0.160 (½−) 0 *Ref*[101]	As-α-2n[100,97,101]; ^{74}Se-α-p[98]; ^{76}Se-d-n[98,99]; parent ^{77}Se m[101,102]	$^{77}_{35}$Br
	0·108, 0·046 spect conv[105]		As-α-n[103,97]; Se-d-n[103]; Se-p-n[106,105]; Br-γ-n[107,62], Br-n-2n[108]	^{78}Br
		^{79}Br, I = $\frac{3}{2}$[38]		^{79}Br
	0·049, 0·037 (e/γ ~ 1·3) ion ch[112]; 0·048, 0·036 spect conv[113]; 0·049, 0·037 spect conv[105]; 0·049 (L_I/L_{III} 1·0) spect conv[114]; 0·48 (e/γ very large) 0·037 (e/γ ~1) abs[115]; others[116]	See ^{80}Br	Se-d-2n[98,99], Se-α-p[98], Se-p-n[106,105,99], Br-n-γ[117,103,110,118,48]; Br-d-p[103]; Br-γ-n[62]; Br-n-2n[30]; spall-fission Ta[119] Bi[120], U[121], fission Th[?,122,123]	^{80m}Br

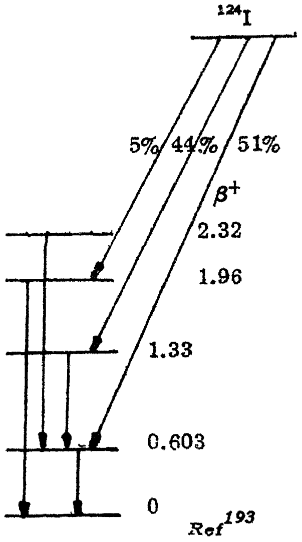
Isotope	Class and identification	Per cent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles
$^{80}_{35}$Br	A chem, n-capt[76]; chem excit, cross bomb[103]. chem, genet[110]		$\beta^-\sim$92%, $\beta^+\sim$3%, EC$\sim$5% (calc from 111,124) β^+/β^- 0·037[111]; $\frac{\beta^+ + \mathrm{EC}}{\beta^-}$ 0·09[124]; β^+/β^- 0·028[125]; β^+/β^- 0·03[126]	18 m[103,110]	β^-: 1·99 (85%), 1·1 (15%) spect[127]; 1·97 (80%), 1·1 (11%), 0·7 (9%) spect[99]; 1·99 spect[113]; others[125,128,117] β^+: 0·87 spect[125]; 1·0 spect[129]; 0·73 abs[126]
^{81}Br		49·48[109]			
^{82}Br	A chem, n-capt[134] chem, excit, cross bomb[103]		β^-[134]; no EC or β^+ (lim 0·03%)[124] no β^+ (lim 0·02%)[111]	35·87 h[78]; 36·0 h[135]; 35·1 h[136]; 35·7 h[137]	0·465 spect, β-γ coinc[138,139]

	Radiation energy, MeV. γ-Transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
	> 0·6 abs[130]; < 0·5 abs[103,106]; no γ[127]	Q^-_β 2·0[99]  ^{80m}Br (5−) 0.086 (2−) 0.037 ^{80}Br (1+) 0 EC β^+ β^- 0.9 (0+) (0+) 0 Ref[131,13]	Se-p-n[106]; Br-n-γ[103,118,48,132]; Br-d-p[103]; Br-γ-n[62]; Br-n-2n[30]; daughter ^{80m}Br[110,130,133]	$^{80}_{35}$Br
		^{81}Br, I = $\frac{3}{2}$[38]		^{81}Br
	γ_1 0·547, γ_2 0·608, γ_3 0·692, γ_4 0·766, γ_5 0·823, γ_6 1·031, γ_7 1·312 spect conv, spect[140], γ_1 0·535, γ_2 0·602, γ_4 0·750, γ_6 1·020, γ_7 1·292, γ_8 1·445 ($\gamma_1/\gamma_4/\gamma_6/\gamma_7/\gamma_8$ ≈ 3·7/3·5/1·0/0·85/0·40) spect[141]; 0·547, 0·615, 0·682, 0·752, 0·822, 1·026, 1·306, 1·453 spect[142]; 1·7 - 2·0 (0·14%) Be-γ-n reaction[88]; 0·07, 0·05 abs conv[143]; others[144]		Se-p-n[106,145]; Se-d-2n[103,146]; Br-n-γ[134,103,48]; Br-d-p[103,146]; Rb-n-α[103]; spall-fission Ta[119], Hg[147], Tl[148], Pb[149], Bi[120,150,151], U[152,121] fission U[153]	^{82}Br

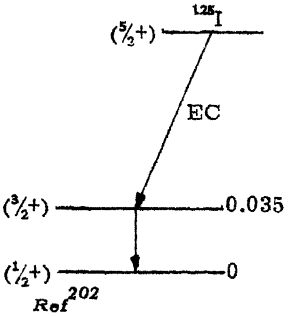
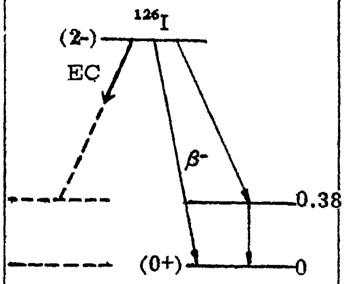
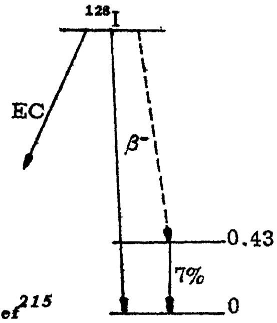
Isotope	Class and identification	Per cent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles	
$^{83}_{35}$Br	A chem, excit[103]		β^- [103]	2·33 h[155, 156]; 2·4 h[157, 130];	0·940 spect[158]; 0·94 spect[99]	
^{84}Br	A chem[169]; chem, excit[170]		β^- [169]	30 m[164]; 32 m[158]; 33 m[171]	4·68 (40%), 3·56 (9%), 2·53 (16%), 1·72 (35%) spect[158]	
^{85}Br	A chem[164]; chem, genet[176]		β^- [164]	3·00 m[177]; 3·0 m[164, 170]	2·5 abs[177]	
^{87}Br	A chem[164,178]; chem, genet[170,177]		β^-, β^- n (~2% of disintegrations) [179]	55·6 s (n)[180]; 55·0 s (n)[181]; 56·1 s (β^-)[177]	β^-: 2·6 (70%), 8·0 (30%) abs[182]; n (mean): 0·25 abs paraffin[180]; 0·30 p recoil in cl ch[183]	
^{88}Br	A chem, genet[177]		β^- [177]	15·5 s[177]		

Radiation energy, MeV. γ-Transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
no $\gamma^{103,157}$; $\sim$0.046 (?) cl ch^{159}		Se-d-n^{103,99}; Rb-γ-α^{156}; spall-fission Ta^{110}, Hg^{147}, Pb^{149}, Bi^{150,151,120}, Th^{160}, U^{152}; fission Th^{161,155,162,163} U^{155,164,165,157}, ^{233}U^{166}, Pu^{167,168}, daughter ^{83}Se, parent ^{83m}Kr^{155,164,165,157}	$^{83}_{35}$Br
0.89, 1.89 scint spect^{172}		Rb-n-α^{170}; spall fission Bi^{149}, U^{121}; fission Th^{163}, U^{169,173,174,164,165,170,171}; daughter ^{84}Se^{175}	^{84}Br
no γ^{177}		fission U^{164,170,176,177}; parent ^{85}Kr^{176,177}	^{85}Br
5.4, others $\sim$3 abs, abs sec, γ-γ-coinc^{182}	Q_{β}^{-} $\sim$8 (?)^{182}  ^{87}Br ($^3/_2$−) β^- 70% ($^1/_2$,$^3/_2$−) 5.4 30% ^{87}Kr ($^5/_2$+) (0+) n ^{86}Kr 0 Ref^{182}	fission U^{164,178,184,177}, ^{235}U^{181,180}, Pu^{181}; parent ^{87}Kr^{170,176,177}; parent ^{86}Kr (2% of dis)^{178,177}	^{87}Br
		fission U, parent ^{88}Kr^{177}	^{88}Br

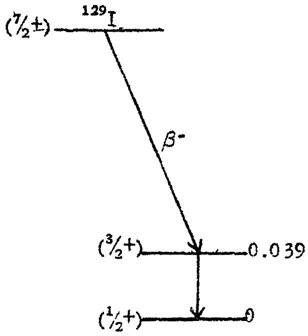
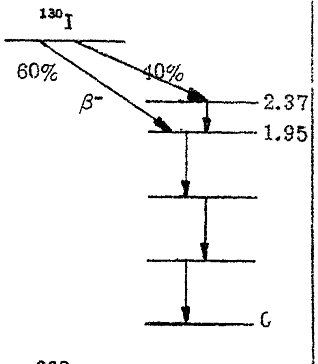
Isotope	Class and identification	Per cent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles	
$^{39}_{35}$Br	D chem[184]		β^-, β^-n [185,180]	4·51 s (n)[180]; 4·45 s (n)[181]	n (mean): 0·43 abs paraffin[180], 0·65 p recoil in cl ch[183]	
$^{120}_{53}$I	D chem[187]		β^+ [187]	30 m[187]	4·0 abs, spect[187]	
^{121}I	B chem, genet[187]		β^+ [187]	1·5 h[189]; 1·8 h[187]	1·2 abs, spect[187]; 1·2, 4·0 (weak)[189]; conv: 0·185 spect[187]	
^{122}I	A chem, excit[187]; sep isotopes[192]		β^+ [187]	3·6 m[192]; 3·4 m[189]; 4 m[187]	2·9 abs[187]; 3·1 abs[192]	
^{123}I	A chem, excit[187]; chem, sep isotopes[193]		EC[187]	13·0 h[193]; 13 h[187]		
^{124}I	A chem, excit, cross bomb[194]		EC ~70%, β^+ ~30% [187]	4·5 d[187]; 4·0 d[194, 195]	2·20 (51%), 1·50 (44%), 0·7 (5%) spect[193]; 2·1 spect, abs[187]	

	Radiation energy, MeV. γ-Transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
			fission U[184,185,177] ^{235}U[181,180]; parent ^{89}Kr (?), parent ^{88}Kr (?)[186]	$^{89}_{35}$Br
			spall Sn (second order reaction)[188]; Sb-α-5n[187]	$^{120}_{53}$I
			spall Sn (second order reaction)[188]; Sb-α-4n, parent ^{121}Te[187]; daughter ^{121}Xe[190,191,189]	^{121}I
			Sb-α-3n[187]; ^{122}Te-p-n[192]; daughter ^{122}Xe[190,191,189]	^{122}I
	0·159 spect, spect conv[193]		spall Sn (second order reaction)[188]; Sb-α-2n[187]; ^{121}Sb-α-2n[193]; daughter ^{123}Xe[190,191,189]	^{123}I
	0.603, 0·73, 1·72, 1·95 spect, spect conv[193]; no γ coinc with 2·2 β^+, β-γ coinc[196]; γ-γ, β-γ coinc[197]	See[131,13]  ^{124}I 5% 44% 51% β^+ 2.32 1.96 1.33 0.603 0 Ref[193]	spall Sn (second order reaction)[188]; Sb-α-n[194,187]; Sb-α-3n.[187]; ^{121}Sb-α-n[187]; Te-p-n[195]; spall-fission Bi[151,120]	^{124}I

Isotope	Class and identification	Per cent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles
$^{125}_{53}$I	A chem[198], chem, excit[199]; genet[200]		EC (L/K 0·23)[201]; EC (L/K 0·3)[202]; no β^+[199]	60.0 d[202]; 56·d[198]	
^{126}I	A excit[205]; chem, excit, cross bomb[194]		EC ~58%, β^- ~40%, β^+ (?) ~2%[206]	13·0 d[194]; 13 d[205]	β^-: 1·268 (27%), 0·85 (73%) spect[193]; 1·24 (~25%), 0·85 (~75%) spect[206]; 0·865 spect[207]
^{127}I		100[212]			
^{128}I	A chem, n-capt[76]		β^- 95·0%, EC + β^+ 5·0%[124]; EC/β^- 0·063[213]	24·99 m[214]	2·02 spect[215]

Radiation energy, MeV. γ-Transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
0.035 ion ch[202]; 0.0355, no 0.109 γ spect conv[200]	See[203,204,131] Q_{EC} ~0.13 calc[201]  Ref[202]	Sb-α-2n[187]; Te-d-n[198,199]; spall-fission Bi[151,120]; daughter ^{125}Xe[200]; not parent ^{125m}Te (lim 0.05%)[202]	$^{125}_{53}$I
with β^-: 0.382 spect conv, β-γ coinc[206]; 0.395 spect, spect conv[193]; with EC: 0.64 (weak) scint spect, x-γ coinc, γ-γ coinc[206]; others[196]	Q_{β}^{-} 1.27[206]  Refs[206,208]	spall Sn (second order reaction)[188]; Sb-α-n[194,187]; Te-d-n[194]; Te-p-n[195]; I-n-2n[194,205,206]; I-γ-n[209,210,211]; spall-fission Bi[151,120]	^{126}I
	^{127}I, I = 5/2 [38]		^{127}I
0.428 (7%) spect[215]	Q_{β}^{-} 2.0[215]  Ref[215]	I-n-γ[76,205,48,215,132,216]; Te-d-2n[194]; Te-p-n[195]	^{128}I

Isotope	Class and identification	Per cent abundance	Type of decay	Half-life	Radiation, energy, MeV. Particles
$^{129}_{53}I$	A chem, n-capt[217]		β^-[217]	$1{\cdot}72 \times 10^7$ y sp act[218]; 3×10^7 y sp act[219]	0·12 scint spect[201]; 0·12 abs[219]; 0·12 ion ch[220], 0·13 abs[218]
^{130}I	A chem, cross bomb[194]		β^-[194]	12·6 h[194]	1·03 (~60%), 0·61 (~40%) spect[222]

Radiation energy, MeV. γ-Transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
0.039 (coinc with β^-, $e_K/\gamma \sim 6$, K/L $\sim$ 40) ion ch, β-γ coinc[220]	^{129}I, I = 7/2 [38] $Q^-_{\beta} \sim 0.17$ [13]  ^{129}I (7/2±) β^- (3/2+) 0.039 (1/2+) 0 Refs[220,221,131]	fission U[217,219,220]	$^{129}_{53}$I
0.744 (e_K/γ 0.003), 0.667 (e_K/γ 0.004), 0.537 (e_K/γ 0.007), 0.417(coinc with 0.6 β^-, e_K/γ 0.012), ($e_K >> e_L$ for all γ's) spect, spect conv, β-γ, γ-γ coinc[222]	 Refs[222]	Te-d-2n[194]; Te-p-n[195], ^{129}I-n-γ[217]; Cs-n-α[223]	^{130}I

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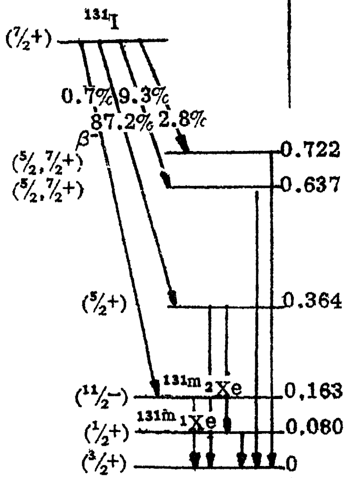
Isotope	Class and identification	Per cent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles	
$^{131}_{53}$I	A chem [194]; chem, genet [224]		β^- [194]	8·141 d [225]; 8·05 d [226]; 8·16 d [227]; 8·04 d [137]	0·815 (0·7%), 0·608 (87·2%), 0·335 (9·3%) 0·250 (2·8%) spect, β-γ coinc [228]; 0·810, 0·606, 0·335, 0·250 spect, β-γ coinc [229]; 0·807, 0·606, 0·339 spect [230]; E (average) 0·189 ion ch [231]; See also: [232,233,234, 235,236,237,238,239, 240,241,242]	
^{132}I	B chem, genet [255]		β^- [255]	2·4 h [255]; 2·3 h [173],	2·2, 0·9 abs [267]; 1·5 abs [268] ~1·4 abs [269]	

Radiation energy, MeV. γ-Transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
0·080 (2·2%, coinc with 0·284 γ, e_K/γ 1·73 K/L 7), 0·163 (coinc with ^{131m_2}Xe) 0·284 (5·3%, coinc with 0·608 β^-, e_K/γ 0·047, K/L 5), 0·364 (80% coinc with 0·608 β^-, e_K/γ 0·018, K/L 8), 0·637 (9%, coinc with 0.335 β^-, e_K/γ 0·0037, K/L 9), 0·722 (3%, coinc with 0·250 β^-, e_K/γ 0·0028, K/L 8) spect, spect conv, β-γ delay coinc, scint spect[228,243] γ_1 0·080133, γ_2 0·28413, γ_3 0·36418 ($\gamma_1/\gamma_2/\gamma_3 \approx$ 5/9/100) cryst spect[244]; γ_2 0·284 (e_K/γ 0·052, K/L 3·3), γ_3 0·364 (e_K/γ 0·021, K/L 5·6), γ_4 0·638 (e_K/γ 0·0040), γ_5 0·723 (e_K/γ 0·0034) ($\gamma_2/\gamma_3/\gamma_4/\gamma_5 \approx$ 6/100/10/3) spect, spect conv[245]; 0·080 (4·3%, with 0·283 γ, e/γ 1·83) γ-γ, x-γ coinc, scint spect[246]; See also: [233,247,232,248,234,237,229,236,239,240,249,241,250,242,230,116,251]	Q^-_β 0·972[228]  ^{131}I (7/2+) 0.7% 9.3% 87.2% 2.8% β^- (5/2, 7/2+) (5/2, 7/2+) (5/2+) (11/2−) (1/2+) (3/2+) ^{131m}$_2$Xe ^{131m}$_1$Xe 0.722 0.637 0.364 0,163 0,080 0 Refs[228,247]	Te-d-n[194,252]; spall-fission Th[160], U[253,254,121]; fission Th[162], U[255,173,256,257,258]; ^{233}U[259,260,166,261]; ^{235}U[259,261], Pu[262]; daughter ^{131}Te[194,255,173,224,263,264]; parent (~1%) ^{131m_2}Xe[249,265]; parent ^{131m_1}Xe[266]	$^{131}_{53}$I
γ_1 0·69, γ_2 1·41, γ_3 2·0 ($\gamma_1/\gamma_2/\gamma_3 \approx$ 37/4/1), γ_4 ~0·8 (very weak) scint spect, γ-γ coinc[270]; 0·6, 1·4 abs[267]		spall-fission U[253,254]; fission Th[163,162], U[255,173,122,256,267], ^{233}U[260]; daughter ^{132}Te[255,173,271,267,272]	^{132}I

Isotope	Class and identification	Per cent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles
$^{133}_{53}$I	A chem ^{255}; chem, genet ^{223}		β^- ^{255,173}	20·5 h ^{226}; 22·4 h ^{273}	1·3 (~91%), 0·4 (~9%) abs ^{274}; 1·4 (~94%), 0·5 (~6%) abs, β-γ coinc ^{275}; 1·4 abs ^{257}
^{134}I	B chem ^{255}; fission fragment range ^{167}		β^- ^{255}	52·5 m ^{273}; 51 m ^{282}; 54 m ^{255}	1·6 (~70%), 2·8 (~30%), hard β (weak) abs ^{274}; 1·5 – 1·75, 3·5 – 4·2 abs ^{282}
$^{135}_{53}$I	A chem, genet ^{285,277}		β^- ^{285,277}	6·68 h ^{276}; 6·7 h ^{286,287}	0·5 (35%), 1·0 (40%), 1·4 (25%) spect ^{276}; 1·4 abs ^{287}; 1·5 abs ^{257}
^{136}I	D chem ^{164}		β^- ^{164}	86 s ^{289}	6·5 abs ^{289}
^{137}I	A chem ^{164,178} chem genet ^{176,177}		β^-, β^-n (~6% of disintegrations) ^{179}	22·0 s (n) ^{180}; 22·5 s (n) ^{181}; 19·3 s genet ^{177}	n (mean): 0·56 abs paraffin ^{180}; 0·67 p recoil in cl ch ^{183}
^{138}I	A chem, genet ^{177}		β^- ^{177}	5·9 s ^{177}	
^{139}I	A chem, genet ^{177}		β^- ^{177}	2·7 s ^{177}	

	Radiation energy, MeV. γ-Transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
	0·53 (94%), 0·85 (5%), 1·4 (1%) scint spect, γ-γ coinc[275]; 0·53 spect[276], 0·55 abs[257]		spall-fission Pb[148], U[253,254]; fission U[255,173,277,223,263,278], Pu[262]; daughter ^{133}Te[255,173,277,223,279,263]; parent ^{133}Xe[277,223,279]; parent (2·4%) ^{133m}Xe[280,281]	$^{133}_{53}$I
	>2·2 (weak) D-γ-n reaction[282]; >1 abs[283]		spall-fission U[253]; fission Th[169], ^{235}U[259,261], U[173,255,122,284,282,283,273], Pu[167,262]; daughter ^{134}Te[173,255,273]	^{134}I
	1·8, 1·27 spect[276]; 1·3 abs[257]; 1·6 abs[287]; 2·4 (1·1%) abs[282]		spall-fission U[254]. fission Th[163] U[277,223,285,279,276,286,287], Pu[262]; daughter ^{135}Te[286,287]; parent (~30%) ^{135m}Xe, parent (~70%) ^{135}Xe[276]; parent ^{135m}Xe[288,279]; parent ^{135}Xe[277,285,288,279]	^{135}I
	1·4, 2·9 scint spect, abs[289,290]		fission U[164,176,289] U[233], Pu[289]	^{136}I
			fission U[164,176,178,181,184,177], Pu[181]; parent ^{137}Xe[176,177]	^{137}I
			fission U, ancestor ^{138}Cs[177]	^{138}I
			fission U, parent ^{139}Xe, ancestor ^{139}Ba[177]	^{139}I

Isotope	Class and identification	Per cent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles
$^{<202}_{85}$At	D chem, excit[291]		α, EC[291]	43 s[291]	6·50 ion ch[291]
$^{<203}$At	D chem, excit[291]		α, EC[291]	1·7 m[291]	6·35 ion ch[291]
^{203}At	D chem, excit[291]		α, EC[291]	7 m[291,97]	6·10 ion ch[291]
^{204}At	B chem, excit, genet[291]		EC[291]	~25 m genet[291]	
^{205}At	B chem, excit, genet[291]		α, EC[291]	25 m[291, 97]	5·90 ion ch[291]
^{206}At	B chem, excit, genet[291]		EC[291]	2.6 h genet[291]	
^{207}At	B chem, excit, genet[292,291]		EC ~90%, α ~10% [292,291]	2·0 h[291]	5·75 ion ch[291]
^{208}At	B chem, excit, genet[291]		EC[291]	6·3 h genet[291]	
^{208}At	A chem, genet[293]		EC 99+%, α 0·5% [293]	1·7 h[293]	5·65 ion ch[293]
^{209}At	B chem, genet, excit[291]		EC ~95%, α ~5% [291]	5·5 h[291]	5·65 ion ch[291]
^{210}At	A chem, excit, genet[296]		EC 99+%, α 0·17% [297], EC 99+%, α 0·1% [298]	8·3 h[296]	5·519 (32%), 5·437 (31%), 5·355 (37%) spect[297]
^{211}At	A chem, excit, genet[299,296]		α 40·9%, EC 59·1% [300]	7·5 h[299, 296]; 7·3 h[301]	5·862 spect[297]; 5·89 ion ch[292,291]

	Radiation energy, MeV. γ-Transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
			Bi-α-spall^{291}	$<^{202}_{85}$At
			Bi-α-spall^{291}	$<^{203}$At
			Bi-α-10n^{291}; Au-C-6n^{97,60}	^{203}At
			Bi-α-9n, parent ^{204}Po^{291}	^{204}At
			Bi-α-8n, parent ^{205}Po^{291}; Au-C-4n^{60,97}	^{205}At
			Bi-α-7n, parent ^{206}Po^{291}	^{206}At
			Bi-α-6n^{292,291}; parent ^{207}Po, parent ^{203}Bi^{291}	^{207}At
			Bi-α-5n, parent ^{208}Po^{291}	^{208}At
			daughter ^{212}Fr, parent ^{208}Po^{293,294}	^{208}At
	0·2, 0·8 scint spect ^{295}		Bi-α-4n, parent ^{209}Po, parent ^{205}Bi^{291}	^{209}At
	0·25, 1·15, 1·40 scint spect^{297}; 1·0 abs, abs conv ^{296}		Bi-α-3n, parent ^{210}Po^{296,291}; parent ^{206}Bi^{298}	^{210}At
		Q_{α} 5·975, Q_{EC} 0·9 est^{302}	Bi-α-2n^{299,303,296,291}; spall Th, U^{304,305}	^{211}At

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Isotope	Class and identification	Per cent abundance	Type of decay	Half-life	Radiation energy, MeV. Particles
$^{212}_{85}$At	E excit[306]		α [306]	0·25 s [306]	
^{213}At	E genet, decay charac [307]		α[307]		9·2 range emuls[307]
^{214}At	B genet[308]		α [308]	~2×10^{-6} s est [309]	8·78 ion ch [308,309]
^{215}At	A genet [310,311]		α[310,311]	~10^{-4} s delay coinc [311, 309], short [310]	8·00 ion ch [311,309], 8·4 ion ch [310]
^{216}At	A genet[311]		α[312,311]	~3×10^{-4} s delay coinc [308, 309]; short (< 54 s) [312]	7·79 ion ch[311,309]; 7·64 ion ch [312]
^{217}At	A genet [313,314]		α[313,314]	0·018 s delay coinc [314, 315]; 0·021 s delay coinc [313]	7·02 ion ch [316]; 7·00 ion ch [314]
^{218}At	E genet[317]		α[317], α 99+%, β⁻ 0·1% [318]	1·5 – 2·0 s [318] several sec (?) [317]	α: 6·63 range[317]; 6·7 ion ch[318]
^{219}At	A chem, genet[319]		α ~97%, β⁻ ~3% [319]	0·9 m[319]	α : 6·27 ion ch [319]

	Radiation energy, MeV. γ-Transitions	Disintegration energy and scheme	Method of production and genetic relationships	Isotope
			Bi-α-n[306]	$^{212}_{85}$At
			descendant ^{225}Pa[307]	^{213}At
		Q_α 8·95, Q_{EC} 1·05 calc[302]	daughter ^{218}Fr[308,309]	^{214}At
		Q_α 8·15, Q^-_β 0·0 calc[302]	daughter ^{219}Fr, parent ^{211}Bi (AcC)[311,309]; natural source, daughter ^{215}Po (AcA), parent ^{211}Bi (AcC)[310]	^{215}At
		Q_α 7·94, Q^-_β 2·03 calc, Q_{EC} 0·46 calc[302]	daughter ^{220}Fr, parent ^{212}Bi (ThC)[311,309]; natural source, parent ^{212}Bi (ThC)[312]; daughter ^{216}Po (ThA)[312]; note ^{216}Po β-stable[13]	^{216}At
		Q_α 7·15, Q^-_β 0·65 calc[302]	daughter ^{221}Fr, parent ^{213}Bi[313,314,315]	^{217}At
		Q_α 6·75, Q^-_β 2·67 calc[302]	natural source, daughter ^{218}Po (RaA), parent ^{214}Bi (RaC)[317,318]	^{218}At
		Q_α 6·39, Q^-_β 1·45 est[302]	natural source, daughter ^{223}Fr (AcK), parent ^{219}Em (An), parent ^{215}Bi[319]	^{219}At

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SECTION XL

THE PREPARATION OF RADIOACTIVE HALOGENS.

By W. J. ARROL

INTRODUCTION

THE n,γ REACTION

Most preparations of radioactive substances are carried out by irradiating target materials with neutrons in a nuclear reactor. Several neutron-induced reactions can be used for production purposes. In the n, γ reaction, a neutron is absorbed in the target nucleus to form a composite nucleus one mass unit heavier than the target and in a highly excited state. It usually passes to the ground state in a very short time with the emission of one or more γ-quanta.[1] The γ-rays arising from this process are usually energetic: for example, those from the capture of neutrons in iron are about 5 MeV. and those from several other elements may reach about 8 MeV.[2,3] In this nuclear process no change of nuclear charge occurs, so that target and product nuclei are chemically the same. The specific activity of an element rendered radioactive by a simple n, γ process is therefore limited. It may be calculated from the relationship:

$$S = \frac{0{\cdot}6 F\sigma}{3{\cdot}7 \times 10^{10} A} \left(1 - e^{-0{\cdot}69 t/T}\right)$$

where

S = specific activity in curies per gram,
F = neutron flux in neutrons per square centimetre per second,
A = atomic weight of the target element,
σ = excitation cross section in barns (1 barn = 10^{-24} sq.cm.),
t = irradiation time,
T = half-life of isotope formed, in the same time unit as for t.

This calculation is conveniently carried out with the aid of a specially designed calculator.[4]

THE n, p REACTION

Another nuclear reaction is the n, p reaction in which the target nucleus absorbs a neutron and emits a proton to give the required nuclide. In this case the nuclear charge of the product is one unit less than that of the target nucleus so that the two are chemically different and the activity could theoretically be separated chemically from the target material and produced truly 'carrier-free'. In fact it is exceedingly difficult to be sure that inactive atoms isotopic with the radioactive product nuclide are not present in the target material, so that the term 'carrier-free' should be used with considerable caution. An example of an n, p reaction is found in the preparation of active phosphorus, ^{32}P, from pile-irradiated elementary sulphur.[5] The product, although of very high specific activity, probably consists of ^{32}P atoms diluted with ^{31}P which was present in traces in the original target sulphur.

The activity to be expected through the *n, p* reaction from the pile irradiation of a target material cannot in general be calculated from the formula used to calculate the specific activity of an element undergoing the *n, γ* reaction, as the meaning of the term 'excitation cross section' is here less precise than in the latter case. The *n, γ* process is usually most efficiently brought about by neutrons which have been slowed by multiple collisions to thermal energies, so that the cross section of a target nuclide to thermal neutrons, which is the effective area of an atom of the nuclide, is measurable and quite well defined even in pile conditions where neutrons of different energies up to more than 1MeV. are present. It may be calculated from mass-energy relationships that most *n, p* reactions will be endothermic. If this is so, there will be a threshold neutron energy below which the reaction will not occur at all, and above this threshold the cross section of the target nuclide for the reaction increases markedly with increase in neutron energy. All that can be done is to irradiate target material in that part of the pile where the highest flux of fast neutrons is present and obtain by experiment some idea of the average cross section for the *n, p* reaction in these conditions. The previously mentioned relationship may then be used for calculating the yield of product activity per gram of target material (S) with different times of irradiation and different neutron fluxes, assuming the energy spectrum of the neutrons to be constant in the different regions of the pile used. The latter condition certainly does not hold at all well, so that the calculation is usually suitable only for estimating the order of magnitude of the activity to be expected, whereas in the case of *n, γ* reactions, the calculated activity yields, for positions in the pile where slow neutron fluxes are known, are usually accurate to about ±20%.

OTHER REACTIONS USED IN PRODUCTION

Another primary neutron-induced reaction is the *n, α* reaction in which a neutron is absorbed into the target nucleus and an α-particle emitted. The product nucleus is of atomic number two less than the target nucleus, so that chemical separation of a very high specific activity material is again possible. In this case, as in the case of the *n, p* reactions, it is usual for the reaction to be endothermic and brought about only by neutrons exceeding a minimal threshold energy.

The fission of uranium-233, uranium-235 or plutonium-239 in the pile results in the formation of large activities of mixed radioactive nuclides. One kilogram of ordinary uranium metal irradiated for a few days at a flux of about 10^{12} neutrons/cm.^{2}-sec. will contain, at pile shut-down, a quantity of the order of 100 curies of mixed fission products. Although much of this activity is short lived, it is possible to extract individual fission products at high specific activity. Even these materials, however, are not truly carrier-free because they are frequently diluted with stable isotopes occurring as the end-products of other fission chains.

There are several cases in which material of high specific activity is made by first carrying out an *n, γ* reaction on a target element to produce an active nuclide of short half-life isotopic with the target element, this isotope then undergoing β-decay to give the required nuclide which is itself radioactive. An example is the preparation of active iodine, ^{131}I, from tellurium. Tellurium-130 (of isotopic abundance 34·4% in natural tellurium) undergoes the *n, γ* reaction to ^{131}Te, which decays by β-emission to ^{131}I. As the β-decay has changed the atomic number, the product nuclide is chemically separable from the target material. Even in this case, however, the product is not truly carrier-free, as traces of ordinary stable iodine are almost always present in the elementary tellurium used for the irradiation and traces of stable and very long lived iodine are also formed from the target tellurium.

A method of producing material of high specific activity by means of the n, γ reaction is the Szilard-Chalmers process.[6] When the composite nucleus resulting from the capture of a neutron gets rid of its excess energy by emission of a high energy γ-quantum, the product nucleus will recoil from this with an energy which may be calculated using the relativistic momentum of the γ-quantum. With γ-rays having energies of the order usually associated with the n, γ reaction, this recoil energy of the product nucleus may be calculated as of the order of several hundred electron volts and therefore much greater than chemical bond energies which are commonly of the order of 1–5 electron volts.[7] Thus, in general, a nucleus undergoing an n, γ reaction will recoil out of the chemical compound in which the element is present as target material and may appear in quite a different chemical form. If the activity in its final chemical form does not exchange rapidly with the same element in the chemical form of the target, chemical separation of the activity from the target element is possible. The ratio of the specific activity of the active material prepared by this process to the activity which would have been obtained by the n, γ process on the ordinary target element is called the enrichment factor for the process. The Szilard-Chalmers process is sometimes of value in pile preparations.[8] It can also be applied to nuclear reactions other than those induced by neutrons.[9] In the pile, with very low neutron doses and with carefully selected Szilard-Chalmers processes, enrichment factors may be as high as 15,000–20,000. The enrichment factor for a given Szilard-Chalmers process falls off with neutron dosage and with other factors, so that for producing in about 100 gms. of target material useful activities of the order of millicuries of a nuclide having a half-life of a few days, a Szilard-Chalmers process giving an enrichment factor of 500–1000 would be about the best that could be expected.

All the production processes outlined above will, almost without exception, produce radioactive nuclides with more neutrons than are required for stability, and they will decay usually by emission of negatively charged β-particles, with or without accompanying γ-radiation. Nuclear reactions are possible with other bombarding particles, and many of these result in neutron deficient radioactive nuclides which will in general decay by positron emission or K-capture. The number of such radioactive materials which are useful for tracer and other purposes is much less than that of those nuclei which decay by ordinary β-emission. The particles of use in such reactions are protons, deuterons and α-particles, and these are produced in cyclotrons and other particle accelerators. High energy γ-rays are produced from linear accelerators and are capable in some cases of giving useful activities through the $\gamma - n$ reaction.

RADIOACTIVE FLUORINE

The only isotope of fluorine which can be used for tracer purposes is ^{18}F which has a half-life of 110 minutes. The isotopes ^{17}F and ^{20}F have half-lives of 70 sec. and 11 sec. respectively, and have not been prepared except for the study of their physical properties. The isotope ^{18}F, which emits positrons mostly of about 0·7 MeV. maximum energy, has been prepared for biological tracer purposes by proton bombardment of the oxygen of distilled water. The nuclear reaction[10] would be $^{18}O(p,n)^{18}F$. This isotope has been used only as fluoride. No Szilard-Chalmers processes are used and no elaborate syntheses have been carried out.

RADIOACTIVE CHLORINE ISOTOPES

CHLORINE – 36

Only two radioactive chlorine isotopes are of interest for tracer purposes:

chlorine–36 and chlorine–38. Chlorine–36 is of half-life about 4×10^5 years and it emits only β-particles of maximum energy 0·714 MeV. The nuclear reactions for its formation are Cl-n-γ and Cl-d-p, so that almost all the production of chlorine–36 is by pile irradiation of chlorine in the chemical form of a simple chloride such as potassium chloride. When chlorine–36 was first prepared, Szilard-Chalmers processes were used, sodium chlorate and sodium perchlorate solutions being the target materials in the Berkeley 37-inch cyclotron. The chlorine–36 was co-precipitated with silver iodide and isolated as sodium chloride. Careful purification, particularly from any traces of sulphur–35 (formed from the reaction ^{35}Cl(n,p)^{35}S), did not change its activity.[11]

Chlorine–36 is most satisfactorily prepared by irradiating potassium chloride in the highest available neutron flux for very long periods, of the order of years. The excitation cross section for chlorine–35 is 43 barns (43×10^{-24} sq.cm.) and its natural isotopic abundance is 75·4%. After one year's irradiation at 10^{13} neutrons/cm.^{2}-sec. ^{36}Cl will be present in natural chlorine to a specific activity of about 250 μc/g. Because of its very long half-life, isotopically pure chlorine–36 will have a specific activity of only about 25 millicuries per gram, so that a specific activity of 250 μc/g. implies the conversion of 1% of the ^{35}Cl to ^{36}Cl.

Activities other than chlorine–36 produced by the neutron irradiation of potassium chloride are:

^{38}Cl by ^{37}Cl $(n,\gamma)^{38}$Cl
^{35}S by ^{35}Cl $(n,p)^{35}$S
^{32}P by ^{35}Cl $(n,\alpha)^{32}$P
^{42}K by ^{41}K $(n,\gamma)^{42}$K

Chlorine–36 may be separated from these by allowing the short-lived ^{38}Cl to decay and then recovering the chlorine from the system by any one of a number of processes, the simplest being to add excess of sulphuric and phosphoric acids to act as hold-back carriers for ^{35}S and ^{32}P, and then to distil off the hydrochloric acid containing the ^{36}Cl. This may be repeated if necessary until the ^{36}Cl is radioactively pure.

Where only low neutron fluxes are available, potassium perchlorate may be used as a target material for the preparation of chlorine–36 by the Szilard-Chalmers process, but there is some doubt as to the wisdom of subjecting perchlorates to high neutron fluxes at pile temperatures above 100°C. for long periods, because of the risk of chemical decomposition.

CHLORINE–38

Chlorine–38 has a half-life of 38 min. and emits β-particles of maximum energies 4·8, 1·1 and 2·8 MeV. and γ-rays of energies 2·1 and 1·6 MeV. It is usually made by the n,γ process on natural chlorine. Chlorine–37 has a natural isotopic abundance of 24·6% and an excitation cross section of 0·61 barns. The irradiation of potassium chloride as target material produces at a flux of 10^{11} neutrons/cm.^{2}-sec. a saturation specific activity of 7 millicuries per gram of chlorine in a few hours. After such an irradiation, the activity of ^{36}Cl is negligible, but ^{42}K, ^{35}S and ^{32}P activities will appear to some extent and may need to be eliminated by the methods indicated above.

RADIOACTIVE BROMINE ISOTOPES

Of the fourteen radioactive bromine isotopes known, only three, bromine–82 and the two isomers of bromine–80, are produced by the pile irradiation of bromine. Bromine–82, with a half-life of 35 hours, is almost always used for tracer and other purposes, and the 4.4 hour ^{80}Br, isomeric with 18 minute

^{80}Br, is usually allowed to decay. Bromine-82 emits β-particles of maximum energy 0·46 MeV. and γ rays having energies ranging from 1·32 to 0·55 MeV. The isotopic abundance of ^{81}Br is 49·48% and the excitation cross section is 2·25 barns. In a week's irradiation at a flux of 10^{11} neutrons/cm.^{2}-sec. the natural mixture of bromine isotopes attains a saturation specific activity of 22 mc/g. The usual target material is potassium bromide or ammonium bromide.

If bromine-82 is required at higher specific activity than is attainable in the highest available pile flux, a Szilard-Chalmers process must be used. The Szilard-Chalmers process with solid potassium bromate as the target material has been extensively studied and can be made to give very large enrichment factors.[12,13] A ninety-fold enrichment is obtained[13] with an irradiation of one half-life at a thermal neutron flux of about 6×10^{11} neutrons/cm.^{2}-sec.

It should, incidentally, be reiterated that the enrichment factor for a Szilard-Chalmers reaction carried out in a pile varies enormously with increased irradiation time. In the case of bromate quoted above, the specific activity of the product fell by a factor of only about 3 when the irradiation time was increased from about one hundredth of a half-life to two or three half-lives. The enrichment factor is the ratio of this specific activity to the specific activity of the pure element irradiated under the same conditions. Because the specific activity induced in the element is small in an irradiation of one hundredth of a half-life, the enrichment factor is very large – in the case of bromate, 22,000. At two half-lives, the enrichment factor had fallen to 47.[13] As in ordinary pile irradiations it is often convenient to irradiate for about one half-life of the radionuclide being produced, the usefulness of a Szilard-Chalmers process might well be assessed by considering the enrichment factor for an irradiation period of about one half-life at maximum available flux.

Other target materials that have been used for Szilard-Chalmers enrichment of bromine include ethyl bromide, ethylene dibromide, bromobenzene, and other organic bromo-compounds.[14-17] In general, organic bromine compounds are less stable under irradiation conditions than is potassium bromate, and the specific activities of ^{82}Br obtainable are consequently lower. A better yield may be obtained by adding aniline to the organic bromo-compound used as irradiation target.[14]

SYNTHESIS BY RECOIL ATOMS

It is possible in some cases to use the recoil energy of a radionuclide formed by an n, γ reaction to carry out a synthesis which would not occur by ordinary thermal means. This has been done both for iodine-128 and for the bromine isotopes 80 and 82.[18-21] In particular, when a mixture of dibromobenzene and acetic acid is irradiated, a large activity of methyl bromide can be recovered at exceedingly high specific activity. In one case a mixture of 180 ml. of acetic acid and 20 ml. of dibromobenzene was irradiated in the thermal column of the British Experimental Pile (B.E.P.O.) at Harwell and the methyl bromide formed was carried out in a hydrogen stream. As much as 50 millicuries of methyl bromide were found to be present although there was not enough material to be visible.[21]

The number of cases where this type of synthesis is possible is limited, and in spite of its ingenuity the method seems unlikely ever to become important.

RADIOACTIVE IODINE ISOTOPES

The only stable iodine isotope is iodine-127. This under neutron bombardment gives rise to the 25-minute isotope iodine-128 through the n, γ reaction. Much of the early work with radioactive iodine and on the Szilard-Chalmers reaction was done on this short lived nuclide which emits β-particles of 1·59 and 2·02 MeV. and γ-rays of energy 0·43 MeV.[6,22] The half-life is so short that this isotope of iodine is not prepared as a routine matter, nor is it of much use for tracer purposes.

A certain amount of work has been done with iodine-130 of half-life 12·6 hours.[23,24] This emits β-particles of maximum energies of 1·03 and 0·61 MeV. and γ-rays of energies 0·75, 0·67, 0·54 and 0·42 MeV. It is prepared in the cyclotron by the reaction ^{130}Te $(d,2n)$ ^{130}I, or preferably by ^{130}Te $(p,n)^{130}$I. The nuclide is not a fission product. As in the case of iodine-128, the half-life of iodine-130 (and also the inconvenience of irradiation in the cyclotron) has led to its being largely abandoned for tracer purposes.

The most generally useful radioactive iodine isotope is iodine-131 of half-life 8·0 days. This has a complex decay scheme. The most energetic β-particles have a maximum energy of 0·815 MeV., though most (87·2%) have a maximum energy of 0·61 MeV. The most energetic γ-rays are of energy 0·722 MeV., though the proportion of these is small.

Recently, iodine-132 of half-life 2·4 hours has been made available in a very convenient chemical device.[25] It emits β-particles of maximum energies 2·2, 1·4 and 0·9 MeV. and γ-rays of 2·0, 1·4 and 0·69 MeV. It is produced in uranium fission as the daughter product of 77-hour tellurium-132. The use of an iodine isotope of such a short half-life is desirable in certain clinical applications where the material is to be administered frequently to a particular patient. It would not normally be feasible to prepare and supply this iodine isotope for use in this way, but a technique has been devised for supplying the 77-hour tellurium-132 in a chemical system from which the daughter iodine-132 can be recovered in the elementary form and used as required. When the apparatus is left after an extraction, the iodine-132 grows again, so that the effective half-life of the source is nearly 77 hours although that of the product is only 2·4 hours.

The parent tellurium-132 is separated from mixed fresh fission products prepared from uranium that has been pile-irradiated for about ten days. The tellurium is dissolved in a eutectic mixture of lithium and potassium chlorides and shipped, as a solid solution of m.p. 365°C., in a small apparatus incorporating a heating furnace. Each time iodine-132 is required, the salt eutectic is melted and air is passed through the melt, carrying the free iodine into any suitable absorbing system. The activity of iodine-132 recoverable from a source of tellurium-132 which was of a known activity at a given time is easily calculable at various intervals after that time, provided the history of previous recoveries is also known.[25]

LARGE SCALE PREPARATION OF IODINE-131

Iodine-131 is by far the most important radioactive isotope of iodine and is used not only as a tracer in biochemical and academic studies but also in medicine for diagnostic and therapeutic purposes. At the present time (1952) world production of iodine-131 may be as high as 25—30 curies per week. For production on the scale of about 5—10 curies per week in a particular laboratory, one of two processes can be used. The first involves the neutron irradiation of tellurium and the second is the production of the fission product iodine-131. Fission product iodine-131 has been produced in the United States since about 1948, and iodine-131 has been prepared from tellurium at Harwell, England since 1949. The second method of production will be described first.

Tellurium-130 is present in natural tellurium in an isotopic abundance of 34·5%. It undergoes the n,γ-reaction to tellurium-131 which has isomers of half-lives 30 hours and 25 minutes, the latter decaying to iodine-131. If natural tellurium as metal is irradiated in the pile at a flux of 10^{12} neutrons/cm.^{2}-sec. for two weeks, it will contain iodine-131 to the extent of about 3 millicuries per gram. As this product differs chemically from the target element

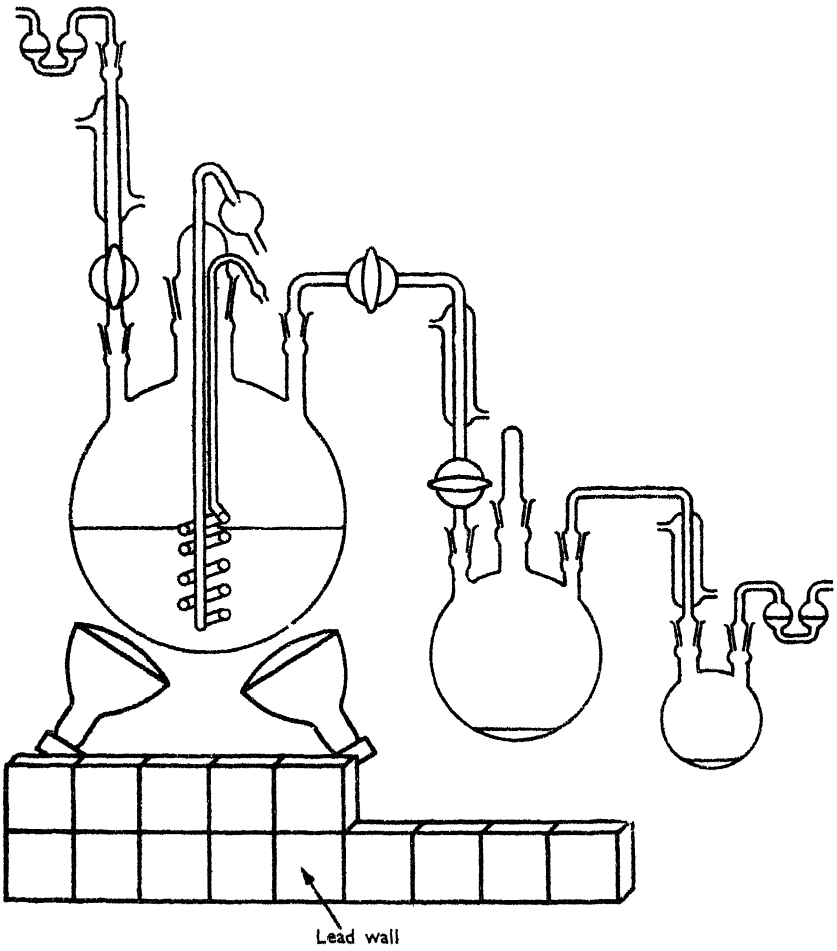

Fig. 1. APPARATUS FOR EXTRACTION OF IODINE-131

it might be thought possible to prepare it truly carrier-free. In fact, *n,y* reactions on tellurium-126 and -128 produce small quantities of stable iodine-127 and the very long lived iodine-129, so that the iodine-131 will be diluted in the ratio of about 1:4. Still more important, however, as a limitation on attainable specific activity, is the fact that all specimens of commercial tellurium metal contain traces of inactive iodine, of the order of 1-100 parts per million. If target tellurium is carefully selected and contains only 2 parts per million of iodine-127, then a fresh solution of iodine-131 prepared from an irradiation at 10^{12} neutrons/cm.^{2}-sec. for two weeks will contain an amount of the order of one microgram of iodine-127 per millicurie of iodine-131, or about 100 atoms of inactive iodine per atom of active iodine.

Levy, Keston and Udenfriend describe a method for recovering iodine-131 from irradiated tellurium by fusion with caustic soda in glass flasks.[26] The iodine passes into the caustic soda phase mostly as iodide, whilst the tellurium is unchanged. This process, whilst giving a high yield, is not suitable for large scale production because of the difficulty inherent in carrying it out by remote control. The earlier method of Livingood and Seaborg is also unsuitable for large scale production.[27] The present general method was first put forward by Perlman, Chaikoff and Morton.[28] It is referred to briefly as that used in Oak Ridge for some time[29] and was later examined in some detail at the Atomic Energy Research Establishment (A.E.R.E.), Harwell.[30,31]

Elementary tellurium is selected for low inactive iodine content and ground to about 40–100 mesh. It is placed in aluminium cans approximately twelve inches long and one inch in diameter, each holding 150 grams. The cans are closed and are irradiated in the pile at a maximum available flux of about 10^{12} neutrons/cm.^{2}-sec. for two weeks. After irradiation, each can contains iodine-131 to the extent of about 400 millicuries, together with a considerably smaller activity due to various radioactive tellurium isotopes. The cans, suitably shielded, are transported to the chemical laboratory for extraction.

The simplest apparatus for extraction is shown in Fig. 1. (see page). It consists of a 5-litre dissolving flask, a receiver which, like the dissolving flask, can also become a distilling flask, and a receiver from which the final distillate can be removed for evaporation. The stopcocks are of large bore, of high vacuum quality, well ground, and ungreased because iodine vapour is rapidly absorbed in grease.

One can of irradiated tellurium is opened and held in tongs. The tellurium is poured into the dissolving flask and is dissolved under reflux in a mixture of chromic and sulphuric acids, the chromic acid being about 50% w./v. and the sulphuric about 50% v./v. Much heat is evolved in this reaction, so it is important that the particle size of the ground tellurium should not be too small or the reaction may get out of control. During this process, the dissolving flask may be heated cautiously with a battery of infra-red lamps, and a spiral of glass tube dips into the solution so that, if necessary, cold water may be passed to retard the reaction. A trap placed above the reflux condenser contains a mixture of sodium hydroxide solution and sodium bisulphite to catch any iodine vapour coming off during the dissolving process. In fact, hardly any activity is ever found in it.

As the tellurium dissolves in the highly oxidizing acid mixture, the iodine-131 appears in solution in the chemical form of iodic acid which is not volatile at about 150°C. In order to distil off the iodine-131, the contents of the dissolving flask are cooled to room temperature and excess of solid oxalic acid is added. This reacts over a period of two hours or so and reduces excess chromium trioxide to chromic ion and iodic acid to iodine, but does not reduce telluric acid as far as elementary tellurium. Then, with the stopcock leading to the reflux condenser closed and those leading to the first receiver open, the iodine is distilled into a trapping solution of sodium hydroxide and sodium bisulphite by which it is reduced to iodide. This first distillate is often too impure for medical and many other purposes: it can contain tellurium, chromic ion and oxalic acid carried over by entrainment. The oxalic acid is destroyed with permanganate which again oxidizes the iodide to iodate. Then a large excess of sulphuric acid is added and the minimum amount of oxalic acid required to destroy excess permanganate and reduce the iodic acid again to iodine. The iodine can then be redistilled and trapped in 10 ml. of 0·01N-sodium hydroxide into which sulphur dioxide has been passed.

After two distillations, the iodine-131 is free from all objectionable impurities. It may happen that traces of sulphuric acid have come over by entrainment and the pH is sometimes as low as 2–3. The solution is raised to the boiling point in an open vessel for two minutes to expel as much sulphur dioxide as possible without losing iodine activity as hydriodic acid. The pH is then adjusted to 8–9 and the solution evaporated down until it contains about 10 millicuries per ml. It is standardized for activity and analysed spectrographically before being dispensed. The overall chemical yield is high, usually above 90%.

Refs. p. 1010

PRODUCTION OF FISSION PRODUCT IODINE-131

It is well known that large activities of fission product iodine-131 are obtained by dissolving irradiated uranium metal in nitric acid and steam-distilling the solution.[29] Working details of this process are unpublished. It is believed that the chemical yield is about 70% and that an output of about ten curies of usable iodine-131 can be made per batch.

CHOICE OF IODINE-131 PRODUCTION METHOD

The two methods of producing iodine-131 in the pile, from fission products and from tellurium, have both advantages and disadvantages. Fission product iodine as usually prepared has as carrier iodine-127 and iodine-129 which occur themselves as fission products, but in a fresh solution the carrier level may not be higher than 20–30 atoms of stable (or near-stable) iodine per atom of iodine-131. The disadvantage of the method is that relatively very large activities of mixed fission products must be handled whilst a given activity of iodine is extracted. Short lived iodine activities must be allowed to decay, and the isotope iodine-133 of half-life 22 hours must have decayed to a negligible relative activity before the 8-day Iodine-131 can be used. This means a decay of about ten days after removal of the irradiated uranium from the pile and even then there may be present between 50 and 100 curies of mixed fission products per curie of usable iodine-131. This means that heavy shielding must be provided and also complete remote handling equipment, which is costly. On the other hand, once the heavy capital expenditure has been made, the production can be carried out by very few and relatively unskilled operators.

In producing iodine from pile-irradiated tellurium, the specific activity is limited by the amount of stable iodine present in the target material. With piles having a maximum flux of around 10^{12} neutrons/cm.^{2}-sec. a production of 10 curies of iodine-131 a week would entail the processing of about 5 kg. of irradiated tellurium powder and this, because of the unpleasant dissolving process, would require a number of small glass plants. On the other hand, almost all the γ-radiation hazard is due to iodine-131 itself, and the shielding problem is relatively slight.

The choice of production method really depends on the available neutron flux. In piles with maximal fluxes of 10^{12} neutrons/cm.^{2}-sec. or less, routine production of large activities of high specific activity iodine would make it necessary to use the fission product method. In piles with an available flux of 10^{13}–10^{14} neutrons/cm.^{2}-sec., a 10 curie per week production could be obtained from 50–500 g. of target tellurium and the processing of this in a single, small apparatus would be safe and straightforward.

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SECTION XLI

CYCLOTRON TARGETS CONTAINING HALOGENS.

By F.D.S. BUTEMENT

In order to withstand the intense local heating produced during the bombardment of a cyclotron target, the halogens have usually been irradiated in the form of compounds which are relatively stable and non-volatile when heated in a vacuum. Certain volatile substances, sealed in thin-walled metal containers, have also been used. Substances used include the fluorides of calcium,[1] sodium or lead,[2] aluminium[3] and barium or caesium,[4] the chlorides of lead,[5] sodium or nickel,[6] lithium,[7] rubidium[8] and potassium,[9] the bromides of sodium, potassium and lead,[10] ammonium bromide[11] and cuprous bromide,[12] the iodides of potassium and lead,[13] ammonium iodide wrapped in aluminium foil and iodine sealed in a platinum capsule.[14]

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SECTION XLII

CHEMICAL USES OF THE RADIOHALOGENS

By C. B. AMPHLETT

Radioactive halogens were much used in chemical studies even before pile-produced nuclides became available; the neutron activation cross-sections of the species ^{37}Cl, ^{79}Br, ^{81}Br and ^{127}I, and the half-lives of the products formed, are such that with the aid of a radium-beryllium neutron source and Szilard-Chalmers enrichment techniques (see page 1106), sufficient activity may be obtained for tracer experiments in any laboratory. More recent developments in nuclear physics have enabled the work to be greatly extended. Many types of investigation have been carried out, some of which could not have been pursued by any other means, e.g. studies of chemical exchange, of equivalence of like atoms in a molecule, and of self-diffusion both in solids and in solution, as well as specific experiments designed to elucidate reaction mechanisms.

A. EXCHANGE REACTIONS INVOLVING RADIOHALOGENS

If an exchange takes place between two atoms of the same element present in two different stable chemical species existing together, e.g. between iodide ion and ethyl iodide, the process will not be observable by ordinary chemical means. If, however, one of the species is initially labelled with radioactive atoms, then the exchange may be followed by separating the two species and measuring the growth of activity in that initially inactive, or the decrease in activity of that initially active, the activities being corrected for radioactive decay during the experiment. The rate thus measured corresponds to the total number of exchanges, both active and inactive. The heat of reaction is negligible, since reactants and products are identical, but the random distribution of nuclides finally established results in an increase in entropy, and hence the free energy change will be negative. The energy of activation is usually quite appreciable, and may be large when unfavourable steric limitations have to be overcome.

The kinetics of simple homogenous exchange reactions were first derived by McKay[1] for the exchange between alkyl iodides and iodide ion in organic solvents, and an independent derivation was later given by Duffield and Calvin.[2] Myers and Prestwood have given a generalized treatment of homogeneous exchange, including the more complex case involving one species containing two atoms of the same element in each molecule which exchange at different rates with the second species.[3] For simple homogeneous exchange the rate of appearance of activity in the initially inactive species is found to obey a simple exponential law; this result is independent of the mechanism of the exchange, of the number of exchanging atoms, and of the specific activity. We can thus speak of an 'exchange half-time' under given conditions, referring to the time taken for the specific activity of either species to change from its initial value to a value half-way towards that corresponding to a random distribution between the two species, corrections for decay being made. Half-times can vary enormously, from complete exchange during mixing and separation to negligible exchange over several days. When exchange is rapid, care must be taken to minimize the possibility of exchange being induced by the separation procedure, and the practical problems involved are fully discussed elsewhere.[3] The kinetics of individual exchange reactions are followed by measuring exchange rates, obtained from exponential exchange plots, under varying conditions of concentration, temperature, acidity, etc., as in normal chemical kinetics.

Heterogeneous exchange is kinetically more complex, since the exponential law is followed only if the re-distribution of activity in the two phases is rapid compared with either the rate of exchange or the rate of diffusion across the interface.[4] This is not usually true for solids, and in a solid-liquid system two stages are observed; the initial rapid exchange involves the surface layers only, and is used to measure specific surface area, while the slow exchange which follows is controlled by the incorporation of the activity into the bulk of the material. This second stage is controlled by factors such as diffusion and recrystallization, and may show dependence upon temperature, solubility, particle size, and lattice defects; much use has been made of this type of exchange to study ionic migration in solids.

Homogeneous and heterogeneous exchange reactions involving the radiohalogens are tabulated in Appendices I and II, which are reproduced, by permission, from more general tables given by Myers and Prestwood.[3] In what follows, the general features of some of these systems are examined in more detail, together with an account of more recent work published up to December, 1953.

The Mechanism of Homogeneous Exchange Reactions

A large number of homogeneous exchange reactions can be shown to proceed by one of two mechanisms, viz:-[5]

(i) Association-controlled exchange: the reactants form a labile association complex, its stability varying for different systems, which on dissociation may give either unchanged reactants or products with exchange. The exchange is controlled by the equilibria:-

$$AX + BX^* \rightleftharpoons [ABXX^*] \rightleftharpoons AX^* + BX,$$

where X^* represents the radioactive atom. Such a process will be bimolecular, with first-order dependence on each of the reactants. The rate-determining step in electron-transfer reactions is usually of this kind, the transfer taking place within the labile transition-state complex.

(ii) Dissociation-controlled exchange: exchange is controlled by dissociation of one of the species, e.g.

$$AX + X^* \rightleftharpoons A + X + X^* \rightleftharpoons AX^* + X;$$

the exchange is unimolecular, of first-order with respect to AX and independent of the concentration of X.

Exchange Reactions in Inorganic Systems.

Apart from fluorine, the halogens and corresponding hydrogen halides exchange rapidly and completely in the vapour phase and in solution. Bromine and hydrogen bromide exchange completely in less than two minutes at room temperature in the vapour phase or in dry carbon tetrachloride;[6-8] chlorine and hydrogen chloride exchange in the vapour phase in the dark, and also in benzene;[9,10] iodine and hydrogen iodide exchange in the vapour phase and in dry pentane.[9,10] Rapid exchange has also been observed between halogens and halide ions in aqueous solution;[11-13,16] in this case the exchange is too rapid for kinetic measurements to be made, and it is usually assumed that the mechanism involves the trihalide ion X_3^-. An attempt was made to measure the rate of the chlorine-chloride exchange by adding acetanilide to the exchange system in 94% water - 6% ethanol,[13] so as to compare the exchange rate with the rate of chlorination of acetanilide, which is itself rapid. Exchange was found to be about one hundred times as fast as the latter reaction. Halford has used this result, together with known data on the chlorination reaction, to estimate a lower limit for the exchange rate, which may be compared with lower and upper limits calculated from thermochemical and equilibrium data for the three possible exchange mechanisms shown below:[14]

$$Cl_2 + Cl^{*-} \rightleftharpoons Cl_3^{*-} \rightleftharpoons ClCl^* + Cl^- \quad (1)$$
$$Cl_2 + H_2O + Cl^{*-} \rightleftharpoons Cl^- + H^+ + HOCl + Cl^{*-} \rightleftharpoons Cl^- + H_2O + ClCl^* \quad (2)$$
$$Cl_2 + OH^- + Cl^{*-} \rightleftharpoons Cl^- + HOCl + Cl^{*-} \rightleftharpoons Cl^- + OH^- + ClCl^*. \quad (3)$$

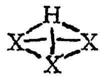
It appears from these considerations that exchange proceeds via the trihalide ion, and this result may be extended to the other halogens with some certainty.

It seems likely that the exchange between halogens and hydrogen halides proceeds by a similar mechanism, involving the intermediate HX_3. The rapid homogeneous gas-phase exchange between bromine and hydrogen bromide was at first thought to involve a chain reaction initiated by bromine atoms arising from the ionization of the gas by the beta-particles, viz.,[8]

$$Br + BrBr^* \rightarrow BrBr + Br^*$$
$$Br^* + HBr \rightarrow HBr^* + Br$$

The rate is, however, unaffected by coating the walls of the vessel with paraffin wax or by painting the vessel black, while a similar exchange rate is observed at an activity level some 20,000 times smaller;[7] it is therefore concluded that the exchange is a simple bimolecular reaction involving the intermediate HBr_3. The exchange between chlorine and hydrogen chloride is largely heterogeneous, the homogeneous component (in vessels coated with a fluorocarbon oil) being very slow.[15] The homogeneous reaction is photocatalyzed, the initial quantum yield for Hg 3650 A. radiation being 110; in this case the exchange is presumably due to a rapid reaction between chlorine atoms on the one hand and chlorine molecules and hydrogen chloride on the other.

The exchange between fluorine and hydrogen fluoride is immeasurably slow at room temperature, either in the dark or when irradiated with a mercury arc, no exchange being observed in thirty minutes for a mixture of 36 cm. hydrogen fluoride and 30 cm. fluorine.[9] A slow exchange at 200°C. was found to be heterogeneous and catalyzed by fluorides of the metal of the vessel employed. In this paper the general question of halide-hydrogen halide exchange is discussed, and it is shown that the observed half-times are much too small for exchange to proceed via thermal dissociation of the halogen, except possibly with iodine, but that exchange would be possible via a complex HX_3 provided that the activation energy for its formation is not greater than 11 kg.-cal.mole^{-1}. Since for exchange to occur the X atoms in HX_3 must be equivalent, it is suggested that the structure of the complex may be



Whichever mechanism is accepted, the rate of the fluorine-hydrogen fluoride exchange will be slow. If it is dissociation-controlled, the high heat of dissociation of fluorine is prohibitive; if association-controlled, several factors militate against the formation of a complex with the above configuration. Fluorine has no electrons in shells higher than the second which could be used in the extra bonding involved, and the strength and polarity of the bond in hydrogen fluoride would probably favour formation of a linear complex of the form F· · · ·H· · · ·F· · · ·F, having non-equivalent fluorine atoms not liable to exchange.

Fluorine and hydrogen fluoride also exchange readily with the interhalogen compounds. The exchange between fluorine and labelled chlorine trifluoride, bromine pentafluoride, or iodine heptafluoride provides an interesting example of the changing balance between two different mechanisms as conditions are altered.[16] In all three cases the rates show a first-order dependence on fluorine concentration and a complex dependence on the halogen fluoride; in the case of chloride trifluoride and iodine heptafluoride the latter dependence changes with increasing temperature over the range 180 – 260°C., while for bromine pentafluoride it is unaltered. The results are explained on the basis of a dual mechanism, viz. (i) a heterogeneous, surface-catalyzed exchange, similar to that between fluorine and hydrogen fluoride, and (ii) a homogeneous gas phase exchange controlled by the dissociation $XF_n \rightleftharpoons XF_{n-2} + F_2$. Bromine pentafluoride, dissociating negligibly over the temperature range studied, exchanges by the first mechanism alone, and the dependence of rate on the concentration of this species is therefore unchanged as the temperature changes. The other two interhalogen compounds dissociate increasingly with increasing temperature, so that the importance of the homogeneous component of the overall rate increases also. By making certain plausible assumptions it has proved possible to separate the overall rate curves into the homogeneous and heterogeneous components and thus to isolate the individual rate constants and activation energies.

The exchange between hydrogen fluoride and a number of halogen fluorides is found to be rapid in both liquid and vapour phases;[17] in the liquid phase it is suggested that it takes place via ionization equilibria of the type

$$HF + IF_5 \rightleftharpoons IF_4^+ + HF_2^-,$$
$$HF + BrF_3 \rightleftharpoons BrF_2^+ + HF_2^-,$$

although the possibility of exchange via association complexes has not been eliminated. Similarly, the rapid exchange of fluorine between chlorine and bromine trifluorides is thought to involve the equilibrium

$$ClF_3 + BrF_3 \rightleftharpoons ClF_2^+ + BrF_4^-;$$

in all these cases the ionization equilibria concerned are those proposed to explain the electrochemical behaviour of these systems. The vapour phase exchange between hydrogen fluoride and the halogen fluorides appears to be largely homogeneous, although it may proceed partly as a heterogeneous exchange catalyzed by fluorides of the metal of the walls (cf. the $HF-F_2$ exchange) and also as a separation-induced exchange on the sodium fluoride used to remove hydrogen fluoride. It is considered that the homogeneous exchange proceeds by an association mechanism involving intermediates of the type $HClF_4$ (with a configuration similar to IF_5) and $HBrF_6$ (similar to IF_7); this would explain why negligible exchange is observed between hydrogen fluoride and either sulphur hexafluoride or dichlorodifluoromethane, since neither sulphur nor carbon has further stable orbitals for association reactions. The fact that iodine heptafluoride also exchanges readily requires the assumption of a different mechanism since the iodine atom already exhibits its maximum covalency; possibly this may involve a dissociation mechanism such as the following:

$$IF_7 \rightleftharpoons IF_5 + F_2$$
$$IF_5 + HF \rightleftharpoons HIF_6$$

The first step is known to lead to rapid and complete exchange of fluorine atoms,[16] while the second is similar to the mechanism proposed above for the other halogen fluorides.

Several studies have been made of exchange in aqueous solution involving oxy-anions of the halogens; in general much longer half-times are found than for halide ions, with values varying from hours to years according to the conditions employed. The exchange between iodine and iodate ion has been most thoroughly investigated: early workers suggested that this must proceed by a specific oxidation-reduction mechanism[18] and subsequent work has enabled the complex mechanism to be elucidated.[19,20] Since iodic acid is a weak acid, the concentration of iodate ion in solutions containing iodic acid depends upon the neutral salt concentration, and the observed iodate ion dependence is different when a neutral salt of an acid other than iodic acid is present. The observed exponents in the rate expression are all fractional, but integral orders are obtained if we assume that exchange proceeds via the equilibrium

$$5I^- + IO_3^- + 6H^+ \rightleftharpoons 3I_2 + 3H_2O.$$

This enables the observed rate law to be converted to a sixth-order expression involving integral powers of all reactants, and comparison is made with other rate laws suggested for the reaction between iodide and iodate ions in acid solution.[21] Although the actual exchange step is not known, it is suggested that it involves the transfer of two electrons between the ions IO_2^+ and I^- present in a transition complex of the type $[IO_2^+, X^-, H^+, I^-]$, where X^- may either be iodate or the anion of the added neutral salt. Exchange between iodine and periodate ion is much slower, and a similar type of mechanism has been suggested, although little experimental work has been done on this system;[22] exchange between iodate and periodate ions is very slow, but is catalyzed by molecular iodine, again suggesting a specific oxidation-reduction mechanism.

Attempts to measure the rate of exchange between bromine and bromate ion lead to difficulties connected with the slow attainment of the equilibria upon which the exchange depends; exchange rates are thus obtained which may also vary according to the method of separation employed.[23] By comparison with the kinetics of reactions involving the oxy-acids of bromine it has proved possible to reveal the causes of the discrepancies, but the determination of the actual exchange rates remains beset with difficulty. Work on the oxy-acids of chlorine has shown that the exchange between chlorine or chloride ion and either hypochlorite, chlorite, or chlorate ion, as well as with dissolved chlorine dioxide, is slow but measurable in acid or neutral solutions.[24,25] On the other hand, chlorine dioxide exchanges very rapidly in solution with either chlorite ion or chlorous acid.

Reference should be made to studies on the exchange of gaseous halogens with inorganic halides, either solid or fused. Two recent papers of interest concern the exchange of bromine with the tetrabromides of the Group IV elements,[26] and with the bromides of some twenty-eight elements distributed throughout the Periodic Table.[27] It is concluded that relatively rapid exchange occurs if the reversible formation of higher bromides is possible, or if specific oxidation-reduction mechanisms are available; for carbon, silicon and tin tetrabromides a parallel is drawn between the extent of exchange and the bond type.

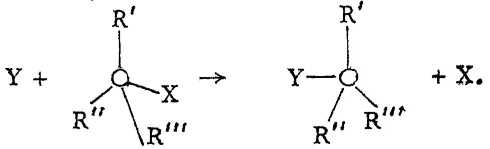
Considerable success has attended the use of radiohalogens in studying the ageing of precipitates. Aged precipitates undergo less exchange with ions present in solution than do freshly-prepared specimens, because in general the specific surface is smaller and the lattice more perfect. Studies with silver bromide and bromide ion, and with silver iodide and iodide ion, have enabled the extent of ageing to be followed;[28-30] similar studies with silver bromide and bromine gas, or with silver bromide and bromine dissolved in ethyl bromide have shown that this precipitate ages very rapidly even under conditions where it is in contact with a medium in which it is insoluble.[31,32] A comparison of the rates of exchange of solid silver bromide with silver ions and with bromide ions has shown that the two processes proceed by different mechanisms. The rate of exchange of silver ion is consistent with a mechanism controlled by diffusion of the ions into the interior of the lattice,[33,34] while the bromide ion exchange is much slower and is markedly reduced by adsorption of dyes on the surface of the precipitate,[28 33] which affects the silver ion exchange only very slightly. It is suggested that bromide ion exchange proceeds via recrystallization, and that silver ion exchange involves diffusion, and possibly also recrystallization. More recent work[35] supports this view, and the results have been used to interpret the lattice structure of silver bromide and to account for certain physical measurements.[36]

Exchange Reactions in Organic Systems.

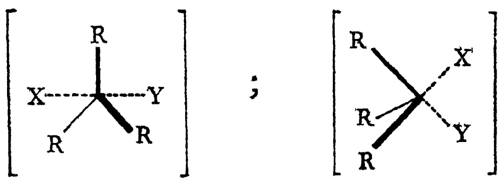
(a) Organic Halide–Halide Ion Exchange.

Exchange reactions between organic and inorganic halides in solvents in which the latter are ionized provide examples of both the types of reaction mechanism discussed above; the exchange may be controlled either by heterolytic dissociation of the organic halide or by formation of an association complex of the type $[RXX^*]^-$. These two mechanisms will be recognized as S_N1 and S_N2 reactions respectively.[37]

S_N2 reactions have been observed in many cases, e.g. ethyl iodide and iodide ion in ethanol,[38-40] bromide ion and *n*-propyl bromide,[41] *n*-butyl bromide,[42] or *iso*butyl bromide[41] in 90% acetone–10% water solution, bromide ion and *iso*propyl bromide, *tert.*-butyl bromide, or 2,4-dinitrobromobenzene in ethylene glycol diacetate solution.[43] The replacement of halogen by halide ion has been used with great success by Hughes and his co-workers in elucidating the mechanism of Walden inversion, in which the substitution of a group Y for a group X in an optically active carbon compound $CR'R''R'''X$ is accompanied by an inversion of the optical configuration. It was suspected,[44] although it could not be proved by purely chemical evidence, that inversion occurred when Y approached the asymmetric carbon atom on the side remote from X, i.e.



If X and Y represent unlabelled and labelled halogen, exchange should be accompanied by racemization, and if the above mechanism is exclusive the rates of racemization and exchange should be equal. This was found to be so for exchange between 2-*n*-octyl iodide, 1-phenylethyl bromide, and α-bromopropionic acid and the corresponding halide ions in dry acetone.[45-47] From these and similar studies it was concluded that bimolecular substitution reactions on an asymmetric carbon atom are always accompanied by inversion; even when optical activity is not involved, the steric course of the reaction will be the same. Ingold has pointed out that energy considerations favour such a mechanism,[37] since the first of the two possible transition states shown below will have a minimum energy, the $CR'R''R'''$ group having a planar configuration.



Graded regularities in the trend of exchange rates have been observed as the nature of the alkyl group is varied in the exchange between iodide ion and alkyl iodides. In ethanol solution the rates decrease in the order methyl>ethyl>*n*-propyl>*n*-butyl, but rise again for *n*-amyl iodide, while branched-chain iodides exchange at considerably lower rates;[38] introduction of a second iodine atom lowers the rate much more than does the substitution of a methyl group. A semi-quantitative treatment of these effects has been given in terms of modern views on steric retardation,[37] by considering the effect of the groups R′, R″, R‴ in CR′R″R‴X upon the transition state and upon the C-X and C-Y bond strengths. The energies of activation of a number of bimolecular exchange reactions have been measured, and usually lie between 18 and 25 kg.-cal.mole^{-1}.[38-42,45-48] Finally, it may be noted that where the inorganic halide is incompletely dissociated, more complex results are obtained; this has been found for exchange between organic iodides and either zinc or cadmium iodide in acetonitrile, and in this case exchange via ionic complexes has been postulated.[48]

The exchange mechanism can sometimes be altered by changing the conditions, and particularly by changing the solvent. Iodide ion exchanges with *tert.*-butyl iodide in alcohol or acetone solution by a bimolecular reaction;[38] in liquid sulphur dioxide the rate is about one to two hundred times as fast, and is moreover independent of iodide ion concentration.[49] The latter exchange is clearly a unimolecular (S_N1) reaction, governed by the rate of ionic dissociation of the alkyl halide, which will be much greater in liquid sulphur dioxide than in the non-ionizing solvents above: the energy of activation, 5·1 kg.-cal.mole^{-1}, is much lower than for the bimolecular exchanges considered above. A similarly exclusive unimolecular exchange has been observed between chloride ion and *tert.*-butyl chloride in formic acid solution.[50] Conflicting results have been obtained with aryl halides and their substituted derivatives; simple S_N2 substitution into the nucleus is not possible, and an S_N1 mechanism based on dissociation of the aryl halide is unlikely.[51] Iodobenzene, *p*-hydroxyphenyl iodide, and *p*-nitrophenyl iodide all exchange by an apparently unimolecular mechanism with iodide ion in 2-octanol, the rate being independent of iodide ion concentration;[52-54] in acetonitrile, which is a more strongly ionizing solvent, a second order exchange was observed for *p*-nitrophenyl iodide.[54] Other workers have found first-order exchange between iodobenzene or *m*-nitrophenyl iodide and iodide ion in acetonitrile, and second-order exchange for *o*- or *p*-nitrophenyl iodide.[55] Further work is required in these cases, since the mechanism is obviously more complex than the examples discussed previously.

Considerable interest arises in the very rapid exchange between halide ion and either allyl iodide,[12,56,59] or allyl bromide,[57] and a completely satisfactory explanation is still lacking. In ethanol solution at 61°C. the measured bimolecular rate constants are 46×10^{-4} l.mole^{-1}sec.$^{-1}$ for allyl bromide[57] and $2{\cdot}13 \times 10^{-4}$ l.mole^{-1}sec.$^{-1}$ for propyl bromide,[58] the energies of activation being 15·5 and 18·0 kg.-cal.mole^{-1} respectively. It has been suggested[3] that the greater ease of exchange for allyl halides is due to the possibility of resonance between the two extreme structures

$$I^{*-} \cdots CH_2{=}CH{-}CH_2{-}I \text{ and } I^*{-}CH_2{-}CH{=}CH_2 \cdots I^-,$$

and the lower activation energy for the allyl halide exchange is considered to reflect hyperconjugation in allyl derivatives.[56] It is obvious that in this case there is a possibility of a bimolecular exchange not involving an S_N2 mechanism, the incoming and outgoing iodine atoms being bound to different carbon atoms; this substitution will be aided by the presence of a double bond in the carbon chain, which can facilitate electron-transfer by a resonance mechanism. It will be seen later that similarly enhanced rates are found for exchange between allyl iodide and molecular iodine.

(b) Organic Halide–Halogen Exchange.

Many systems of this type have been studied in the vapour and liquid phases as well as in solution; exchange occurs usually, although not exclusively, via the formation of halogen atoms, either by thermal or photochemical dissociation of the halogen. The first studies reported no exchange between iodine and methyl iodide at room temperature in alcoholic solution or at 100°C. in the absence of a solvent, but exchange was complete in fifteen minutes in alcoholic solution at 100°C.[59]

Among other systems studied are the exchange reactions between iodine and di-iodoethylene, allyl iodide, and iodobenzene.[60-62] Both the thermal and photochemically-initiated exchanges with *cis*- and *trans*-di-iodoethylene have been investigated, and they have been compared with the iodine atom-initiated isomerization reaction between the *cis*- and *trans*-forms, all in saturated hydrocarbon solvents.[60-62] The exchange and isomerization reactions show the same dependence upon iodine concentration and absorbed light intensity, indicating the participation of iodine atoms; the exchange reaction is, however, more than one hundred times as fast as isomerization, the respective activation energies being 8 and 12 kg.-cal.mole^{-1}, so that exchange must occur without appreciable isomerization and by a different mechanism.

Allyl iodide exchanges more than two hundred times as fast as di-iodoethylene, and the former has been studied in some detail.[63,64] The thermal exchange is unique in that in hydrocarbon solvents at room temperature most of the exchange appears to involve molecular, and not atomic iodine; exchange is very rapid, with an activation energy of 13·1 kg.-cal.mole^{-1}. The authors suggest that exchange occurs by interaction of iodine with the double bond, the transition complex $C_3H_5I_3$ being related to the unknown glyceryl tri-iodide for which there are two possible structures. The photochemical exchange is a complex chain process, in which the presence of oxygen leads to chain-termination by a slower, simultaneous oxidation mechanism. The data have been fitted to a complex rate expression which indicates that at 25°C. the rates of exchange of iodine atoms with iodine molecules, allyl iodide, and di-iodoethylene are in the ratios 32,000 : 2,000 : 1. It is suggested that the approaching iodine atom attacks the end of the molecule remote from the outgoing iodine atom, but there is no concrete evidence for this. In the related exchange between allyl bromide and bromine atoms, exchange is accompanied by isomerization to give a mixture of the three bromopropenes.[65,66] All three undergo isomerization on exchange, and the proportions of the final products appear to be independent of the starting material, e.g. a 1% solution in bromobenzene in presence of air gives 22% 1-bromo-, 3% 2-bromo-, and 75% 3-bromopropene. These effects have been explained in terms of proton and electron transfer in the intermediate radical $C_3H_5Br_2$ formed by addition of a bromine atom to the original compound.

Exchange reactions between iodine and organic iodides have been reviewed by Noyes and Sibbett,[67] who distinguish two types, both initiated by iodine atoms. Direct substitution, viz. $RI + I^* \rightarrow RI^* + I$, followed by other reactions of atomic and molecular iodine, is considered to take place with olefinic, allylic and aryl iodides, where the electrons of the unsaturated system are available to the approaching iodine atom. The alternative mechanism involves formation of a free radical by the step $RI + I^* \rightarrow R\cdot + II^*$, followed by $R\cdot + II^* \rightarrow RI^* + I$ and other reactions; this is considered likely for the slow reactions involving alkyl iodides, and may occur to some extent with allyl iodide also. The evidence available on benzyl iodide suggests that this behaves as a typically aliphatic iodide, the aromatic nature being completely screened by the side-chain; this system is kinetically more complex, however, since at 80°C. the degree of dissociation of benzyl iodide is comparable with that of iodine, so that chains may be initiated either by iodine atoms or by benzyl radicals.[68]

Exchange between bromine and carbon tetrabromide has been studied in the gas phase (170 - 200°C.) and in the liquid phase (107 - 160°C.);[69] in both cases the same mechanism appears to hold for molar ratios of reactants between 0·1 and 10·0. The homogeneous reaction has a rate given by the expression $R = k[\mathrm{CBr_4}][\mathrm{Br_2}]^{0\cdot5}$, indicating a rate-controlling reaction between bromine atoms and carbon tetrabromide molecules. Using values of bromine atom concentration calculated from the bromine dissociation equilibrium, activation energies of 3 kg.-cal.mole^{-1} for the liquid phase and zero for the gas phase were calculated, but these figures are not very significant; steric factors of $10^{-4} - 10^{-5}$ were calculated by comparison with collision theory.

The exchange between bromine and bromotrichloromethane has been studied independently by two groups of workers,[70,71] in the vapour phase (150 - 220°C.) and in the liquid phase (100 - 170°C.); earlier work had indicated a photochemical exchange in carbon tetrachloride solution at 76°C.[72] The rate is proportional to the product $[\mathrm{CCl_3Br}][\mathrm{Br}]^{1/2}$, the activation energy for the initiating reaction $\mathrm{CCl_3Br + Br^* \rightarrow CCl_3Br^* + Br}$ being estimated[70] as 7 and[71] 10·3 kg.-cal.mole^{-1}. The observed rates do not enable a distinction to be made between the two types of mechanism described by Noyes and Sibbett (loc.cit.), viz.

$$\begin{array}{rl} & \mathrm{Br^* + CCl_3Br \rightarrow Br^*CCl_3 + Br,} \\ \text{and} & \left.\begin{array}{l}\mathrm{Br^* + CCl_3Br \rightarrow Br^*Br + CCl_3\cdot} \\ \mathrm{CCl_3\cdot + Br^*Br \rightarrow CCl_3Br^* + Br}\end{array}\right\}. \end{array}$$

Data on the photobromination of chloroform[73] suggest that the reactions $\mathrm{CCl_3\cdot + HBr \rightarrow CHCl_3 + Br}$ and $\mathrm{CCl_3\cdot + Br_2 \rightarrow CCl_3Br + Br}$ are similar in rate, and it was found[71] that in a mixture of hydrogen bromide, bromine, and bromotrichloromethane, chloroform was formed at a rate comparable to the exchange rate at the same temperature; this was taken to indicate the second mechanism, involving $\mathrm{CCl_3\cdot}$ radicals.

(c) Exchange with Aluminium Halides and other Metal Halides.

The use of aluminium halides in the Friedel-Crafts synthesis is well-known, and many other metallic bromides are used as catalysts in organic bromination reactions. Exchange studies have been carried out in an attempt to elucidate the mechanism of such reactions, and a variety of results has been obtained, as set out in the appended tables. In the Friedel-Crafts reaction, viz:-

$$\mathrm{ArH + RX + AlX_3 \rightarrow Ar.R + HX + AlX_3,}$$

where Ar is an aryl radical, R another radical, and X may be either Br or Cl, one possible mechanism involves the formation of the carbonium ion $\mathrm{R^+}$:-

$$\begin{array}{l} \mathrm{RX + AlX_3 \rightleftharpoons R^+ + AlX_4^-} \\ \mathrm{ArH + R^+ \rightarrow Ar.R + H^+} \\ \mathrm{H^+ + AlX_4^- \rightleftharpoons HX + AlX_3.} \end{array}$$

On the basis of such a mechanism, $\mathrm{AlX_3}$ could exchange with RX and with HX. It was in fact found that acetyl chloride exchanges readily with aluminium chloride, and that the hydrogen chloride produced in the formation of acetophenone from benzene and acetyl chloride in presence of labelled aluminium chloride is itself active;[74] these experiments are, however, not conclusive regarding the mechanism of exchange. Recent work on the exchange between carbon tetrachloride and aluminium chloride has given an insight into the nature of the reaction;[75] it can be shown that the endothermicity of the carbonium ion mechanism is too great for it to be likely in this case. Nevertheless, solid aluminium chloride exchanges rapidly with either liquid carbon tetrachloride or its vapour, both at 25°C. and at the melting-point of the organic liquid; rapid exchange with liquid chloroform is also observed. The mixed vapours do not exchange, and the rate exchange involving solid aluminium chloride is strongly dependent upon the nature of the surface of the latter, partly hydrolyzed material exchanging much less rapidly than a fresh surface which has not been exposed to moisture. The rapid exchange is incomplete except at high temperatures, and the degree of exchange is dependent upon the ratio of the reactant concentrations. These facts suggest the exchange to be a surface reaction, the adsorption of carbon tetrachloride on the surface of the aluminium chloride being followed by exchange during desorption. The effects of surface and concentration ratio are then apparent, while the incomplete exchange at ordinary temperatures is presumably due to a slow redistribution of the activity initially located on the surface after exchange; this mechanism would also explain the rapid exchange at low temperatures. The authors suggest that a similar mechanism may operate in the Friedel-Crafts reaction when the catalyst is insoluble, but that where the latter is soluble a mechanism based on soluble molecular or ionic complexes is likely.

The exchange between aluminium and hydrogen halides has led to conflicting results. Earlier work with aluminium chloride and gaseous hydrogen chloride reported negligible exchange at room temperature, but complete exchange in 76 hours at 213°C.; this was cited as evidence against the formation of the complex $HAlCl_4$, and this view appears to be supported by other physical evidence.[76] More recent work carried out in some detail suggests that complete exchange may be obtained in this system in five minutes at room temperature, and that even at -80°C. exchange is appreciable.[77] The mechanism appears to be similar to that involving carbon tetrachloride, the rate varying with the reactant ratio and with the specific surface of the solid, but with hydrogen chloride the rate is the same for both commercial and freshly-synthesized aluminium chloride. Exchange was very rapid at 100°C., fresh surfaces being continually exposed by sublimation. The discrepancy between these results and the earlier observations is probably due to the great sensitivity of surface reactions to external conditions.

Alkyl halides exchange readily with labelled aluminium halides,[77-79] and the reaction has been suggested as a good means of preparing labelled alkyl halides.[77] It has been shown that for methyl bromide there is a correlation between the extent of exchange and the catalytic activity of the inorganic bromide,[80] e.g. in the series aluminium, barium and potassium bromides, the exchange activation energies are respectively 4·6 and 12 kg.-cal.mole^{-1}, and very high (potassium bromide showing no detectable exchange), while the catalytic effect on reactions of methyl bromide decreases in the above order (potassium bromide being inactive catalytically). Comparative measurements of heats of adsorption of methyl bromide on barium bromide suggest that the rate-determining step in the exchange involves adsorbed methyl bromide and crystals of barium bromide. In general, aluminium halides are considerably more reactive than other inorganic halides in exchange with aryl halides also.[81]

B. THE EQUIVALENCE OF ATOMS IN A MOLECULE

Two methods are possible for testing the equivalence of the atoms X within a molecule AX_n. The molecule may be synthesized from a compound AX_{n-m} and then decomposed again, e.g.

$$PBr_3(l) + Br_2^*(l) \rightarrow PBr_5^* \xrightarrow{heat} PBr_3^*(l) + Br_2(g);$$

if the activity originally present in molecular bromine is not randomly distributed among all the bromine atoms at the end of the experiment, then the five bromine atoms in phosphorus pentabromide are not equivalent. Unfortunately, a random distribution is not an unequivocal proof of equivalence, since there may have been induced exchange during synthesis, after synthesis, or during separation. In all cases so far investigated, e.g. the polyhalides of gold, copper and phosphorus,[82-84] and the ion HgI_4^{--},[85] the interpretation is open to doubt for these reasons. Exchange during synthesis and exchange between halogen and higher halide have been shown to be small for the polyhalides of gold and copper, but the possibility of exchange during decomposition has not been eliminated.

The second method involves the measurement of exchange rate and equilibrium between the species AX_n and X^*; if all the X atoms in AX_n are identical, the exchange rate will be constant and the final equilibrium will correspond to a random distribution of activity. If, however, the observed rate is either negligible or immeasurably fast, no conclusions can be drawn, since, obviously, it is not possible to differentiate between two or more rates which are all either too great or too small to be measured; in addition, there is again the possibility of separation-induced exchange. Consequently, the complete and rapid exchange between labelled bromide ion and the ion $PtBr_4^{--}$ in aqueous solution does not unambiguously indicate equivalence of the bromine atoms,[86] and here recourse must be had to the more laborious methods of structure determination. Until recently only one unequivocal example of this type existed, showing the non-equivalence of the iodine atoms in diphenyliodonium iodide, $(C_6H_5)_2I_2$; on exchanging with labelled iodide ion in hot 50% alcohol only one of the two is replaced, the activity at equilibrium being equally divided between the two species.[87] No exchange is observed between the two iodine atoms in $(C_6H_5)_2I.I^*$ even under conditions leading to appreciable deomposition. These results are in accord with the accepted structure $[(C_6H_5)_2I]^+I^-$. A second example is described briefly in a recent note.[88] Chlorine and phosphorus pentachloride exchange in carbon tetrachloride with a composite rate; the initial exchange is immeasurably fast, and is followed by a normal homogeneous first-order rate. The results accord with the assumption that the rapid exchange involves three chlorine atoms, with a slower, measurable exchange with the other two. By analogy with structural data, which show the five atoms to be non-equivalent, it is suggested that these two exchange rates refer to the three equatorial and the two apical chlorine atoms respectively.

C. THE SELF-DIFFUSION OF IONS IN SOLUTION

The self-diffusion of an ion in solution can only be measured by tracer techniques, since there is no detectable physical or chemical change; such measurements are of value in the interpretation of solution theory. Three methods are in general use, of which the capillary tube technique is that most generally applicable.[89] The tracer is contained in a short capillary tube of uniform bore, closed at one end and mounted vertically below the surface of the inactive solution, which is well stirred and maintained at constant tempera- to minimize convection effects; the mean activity within the capillary is measured as a function of time and the diffusion coefficient *D* measured. By this means the self-diffusion of chloride ion in calcium chloride solution,[90] and of iodide ion in a series of aqueous iodide solutions[91,92] has been measured. In solutions of hydrogen, lithium, sodium, potassium and rubidium iodides it was shown that the values of *D* for iodide ion depend not only upon the viscosity of the solution but also upon a parameter related to the size of the cation;[91] plots of $D\eta/\eta_0$ versus $C^{\frac{1}{2}}$, where C is the solute concentration and η/η_0 the specific viscosity of the solution, give straight lines of increasing negative slope in the order Li^+, $H^+ < Na^+$, $K^+ < Rb^+$. By applying a treatment based upon the Debye–Hückel theory and introducing the 'distance of closest approach' of ions, the points for all the cations could be fitted quite well to one curve. The physical significance of the treatment is that the size of the hydrated cation affects the charge distribution in the ionic atmosphere of the iodide ion, and hence the potential of the latter; the effect of cation radius then follows if the diffusion coefficient is dependent both on the potential of the diffusing ion and on the viscosity of the solution.

The self-diffusion of anions in ion-exchange resins has also been measured, using labelled chloride, bromide, iodide and bromate ions on Dowex-2 (a strong base-exchanger), and labelled bromide ion on Dowex-50 (a cation exchanger).[93,94] In the former case, values of D were of the order $1-5 \times 10^7$ $cm^2 sec^{-1}$ at 25°C., with activation energies of 6 - 9 kg.-cal.mole^{-1} between 0° and 25°C. Values were not so dependent on ionic charge and degree of cross-linking as for cations on cation-exchangers, and suggested that the size of the exchange group largely determines permeation rates. On Dowex-50, bromide ion diffuses more slowly than water molecules, but more rapidly than univalent cations.

D. APPLICATION OF RADIOHALOGENS TO KINETIC STUDIES

Much information has been obtained about the mechanism of chemical reactions by introducing labelled species, and also from exchange studies themselves; thus the exchange between iodine and iodate ion in aqueous solution has led to a better knowledge of the reaction between iodide and iodate ions in acid solution.[20] This has been shown to be a sixth-order reaction, and the results of earlier workers leading to the assumption of fourth- and fifth-order reactions[21] have been attributed to failure to maintain constant ionic strength and to neglect of the weakness of iodic acid in the treatment of the results. It has already been mentioned that tracer studies show that the iodine atom-catalyzed isomerization of di-iodoethylene proceeds by a mechanism different from that of the exchange reaction;[60] from the results on the exchange in hexane solution, approximate figures have been derived for the rate of exchange between iodine atoms and iodine molecules in hexane solution, and also for the primary quantum yield of photodissociation of iodine.[62] The latter was obtained from measurements of chain life, using a rotating sector technique, and is approximately 0·4 - 0·6 at 578 - 536 mμ. The deviation from unity is considered to be due partly to primary recombination of the atoms within the solvent 'cage', and also to secondary recombination of the original atoms in a time short compared with that in which they can diffuse and encounter atoms from different molecules. These values are of course dependent upon the mechanism assumed for the exchange, but are in good agreement with independent values derived from spectrophotometric determinations of the rate of recombination of iodine atoms produced by flash photolysis in heptane and carbon tetrachloride solutions.[95]

Tracer iodine has been used in a variety of kinetic studies. Using labelled iodine-substituted free radicals derived from the dissociation of the hexa-substituted ethanes, e.g. $I.C_6H_4.CR_2.CR_2.C_6H_4I \rightleftharpoons 2\ I.C_6H_4.CR_2\cdot$, it has been shown that when vinyl compounds are polymerized by the action of these radicals the radical itself is incorporated into the polymer, the latter exhibiting activity characteristic of the iodine tracer.[96] Considerable use has been made of radioactive iodine in recent years in trapping free alkyl radicals. Early studies of the decomposition of alkyl iodides showed that free radicals may be converted into stable products by reaction with molecular iodine, viz:-

$$R\cdot + I_2 \rightarrow RI + I.$$

By using labelled iodine in such an exchange and adding afterwards a mixture of carrier alkyl iodides which may be separated by fractional distillation, each will carry with it the corresponding labelled iodide if formed. The presence of activity in a given fraction is, therefore, a strong indication of the presence of the appropriate radical in the initial products, and a quantitative estimate may also be made if the efficiency of the recovery procedure is known. In this way the traces of liquid products formed from photolysis or radiolysis of liquid alkyl iodides may be identified; e.g. *cyclo*hexyl iodide has been found when methyl iodide is photolyzed in *cyclo*hexane solution.[97] The radiolysis of alkyl iodides and of alkanes in both the liquid and gaseous states has been studied by this means, and the distribution of activity between the alkyl iodide fractions found.[98] Bonds between carbon and iodine were more readily broken than those between carbon and hydrogen, as would be expected; the relative yield of methyl iodide decreases with increasing chain-length. More recent work has detected traces of ethyl iodide and methylene di-iodide in the products from the decomposition of liquid methyl iodide by either ultra-violet light or *X*-radiation.[90-101] The exchange induced by electron radiation between iodine and both methyl and ethyl iodides has been followed by measuring the decrease in iodine activity, without attempting to identify the products;[100] in this case a similar exchange was found when mixtures of bromobenzene and labelled bromine were irradiated with fast electrons.

A somewhat different application is found in the field of ketone photolysis, where labelled iodine has been used to remove the radicals formed in the primary act, and so to enable the primary quantum yield to be calculated.[102] The primary process comprises two individual steps, both for acetone and for methyl ethyl ketone; complications arise in the former case because iodine exerts a specific deactivating effect on one of the excited molecules involved, the primary quantum yield being dependent on the iodine pressure.

With the aid of tracer bromine it has been shown that bromine atoms replace hydrogen atoms in naphthalene seven times more rapidly than in benzene,[106] and that in the formation of ethyl bromide from ethylene and hydrogen bromide, polymerization of ethylene is an important side-reaction;[103] the forward and reverse reactions in the equilibrium $C_2H_4 + HBr \rightleftharpoons C_2H_5Br$ have also been studied.[105]

Labelled chlorine has been used extensively. Investigations of the conversion of camphene hydrochloride to *iso*bornyl chloride in the presence of labelled deuterium chloride showed that ionization of the hydrochloride is rapid, the rate-determining step being a bimolecular reaction between the positive ion so formed and a molecule of hydrogen chloride. If the latter reaction is assumed to be accompanied by inversion, the stereochemistry of the reaction may be explained and the configuration of the product determined.[103] In the inorganic field a comprehensive investigation has been made of reactions involving different oxidation states of chlorine in aqueous solution, viz:-[24,25]

$$
\begin{aligned}
&Cl_2 + 2HClO_2 \rightarrow 2ClO_2 + 2Cl^- + 2H^+\\
&HClO + 2ClO_2^- \rightarrow 2ClO_2 + Cl^- + OH^-\\
&HClO + ClO_2^- \rightarrow ClO_3^- + Cl^- + H^+\\
&4H^+ + 2Cl^- + 2ClO_3^- \rightarrow Cl_2 + 2ClO_2 + 2H_2O\\
&5HClO_2 \rightarrow 4ClO_2 + Cl^- + H^+ + 2H_2O \text{ (catalyzed by } Cl^-\text{)}
\end{aligned}
$$

In all these cases, virtually all the chlorine dioxide or chlorate produced arises from chlorous acid or chlorite; only about 5% of the activity initially present as chlorine, hypochlorous acid, or chloride appears finally as chlorine dioxide or chlorate, and even this may be traced to side-reactions. This appears to indicate that the reactions involve an unsymmetrical intermediate, e.g.

$$Cl_2^* + ClO_2^- \rightarrow Cl^*.ClO_2 + Cl^{*-}$$

or $H^+ + HOCl^* + ClO_2^- \rightarrow Cl^*.ClO_2 + H_2O$,
followed by $2Cl^*.ClO_2 \rightarrow Cl_2^* + 2ClO_2$
or $Cl^*.ClO_2 + H_2O \rightarrow Cl^{*-} + ClO_3^- + 2H^+$,

and similarly in the other cases. A similar result has been obtained in the reaction

$$2H^+ + 2I^- + IO_4^- \rightarrow I_2 + IO_3^- + H_2O,$$

labelled iodide being converted to labelled iodine, the iodate fraction being inactive.[104]

Although strictly outside the kinetic field, reference should be made to the use of labelled iodine in determining the solubility of solid p-chloroiodobenzene in compressed ethylene gas between 13° and 31·5°C. and at pressures up to 100 atm., since this technique makes possible a new range of physical measurements.[107] The solute was synthesized with ^{131}I incorporated into the molecule, and a weighed amount placed at the bottom of a duralumin bomb maintained at the required temperature and pressure. The gas phase was stirred with a magnetically-operated spiral stirrer and its activity measured by means of a Geiger counter mounted outside the bomb and shielded from direct radiation from the solid; by this means the volume concentration of the solid in the gas phase could be measured to ± 2·4%.

TABLES OF HOMOGENEOUS AND HETEROGENEOUS ISOTOPIC EXCHANGE REACTIONS

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Notes: The following abbreviations are employed: (g) gas phase, (l) liquid phase, (s) solid phase, (aq) aqueous phase, *f* gram formula weight per litre, meas measurable, Rm room temperature, ext extracted, mmole millimole, a.l. atomic or molecular layers. Seconds, minutes, hours, days andnyears are indicated respectively by s, m, h, d, y.

Italicized half-times are believed to be reliable for one of the following reasons:-

(1) Measurable exchange rates were obtained that obeyed the exponential exchange law.
(2) Immeasurably small exchange rates were obtained from experiments in which first one then the other reactant was tagged or in which good recovery of the radioactivity and reactants was reported.
(3) Immeasurably large exchange rates were obtained from experiments in which the reactants were separated by a method believed to cause no separation-induced exchange.

ISOTOPIC EXCHANGE REACTIONS

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ISOTOPIC EXCHANGE REACTIONS – HOMOGENEOUS

Element and Tracer	Reactants	Temp. °C.	Other Conditions	Separation Method	Half-Time of Exchange	Lit. Ref.
^{18}F (112 m.)†	F_2 – HF*	24	46 cm. F_2(g), 31 cm. HF(g), dark.	HF(s)	*Very long*	9
^{18}F (112 m.)	F_2 – HF*	24	30 cm. F_2(g), 36 cm. HF(g), illuminated with Hg arc.	HF(s)	*Very long*	9
^{18}F (112 m.)	F_2 – HF*	100 – 140	38 cm. F_2(g), 36 cm. HF(g), dark.	HF(s)	*Very long*	9
^{18}F (112 m.)	F_2 – HF*	190	38 cm. F_2(g), 35 cm. HF(g), dark.	HF(s)	*>6 h.*	9
^{18}F (112 m.)	F_2 – HF*	210	38 cm. F_2(g), 36 cm. HF(g), dark. (All gas pressures measured at 24°C.)	HF(s)	*~3·5 h.*	9
^{38}Cl (38 m.)	Cl_2 – Cl^{*-}	. . .	0·06 *f* acetanilide, 0·15 *f* NaCl, 0·5 *f* H_2SO_4, $\ll$0·012 *f* Cl_2	Chloroacetanilide(s)	$<10^{-3}$ *s.*	13,14
^{38}Cl (38 m.)	Cl_2 – HCl*	. . .	0·40 *f p*-chlorophenol, 0·00960 *f* HCl, $\ll$0·00365 *f* Cl_2 in benzene	Chlorinated phenol(s)	Very short	10
^{38}Cl (38 m.)	Cl_2^*(g) – HCl(g)	25	27·5 cm. Cl_2, 47·9 cm. HCl, dark.	Cl_2(s)	<6 m.	9
^{38}Cl (38 m.)	Cl^*O_2 – Cl_2	25	0·043 *f* ClO_2, 0·028 *f* Cl_2, 0·06 *f* HCl.	ClO_2 in CCl_4 (Cl_2 ext. from CCl_4 by Cl^-, $HPO_4^=$)	*>4 h.*	24
^{38}Cl (38 m.)	Cl^*O_2 – Cl^-	25	0·035 *f* ClO_2, 0·1 *f* NaCl, 0·05 *f* $HClO_4$ or *p*H 7·2.	ClO_2 in CCl_4	*>4 h.*	24
^{38}Cl (38 m.)	ClO_2 – Cl^{*-}, Cl^*O^-	25	0·022 *f* ClO_2, 0·031 *f* NaCl, 0·031 *f* HClO, *p*H 6·2 (oxidation of ClO_2 faster than exchange).	ClO_2 in CCl_4	*~4 h.*	24

^{38}Cl (38 m.)	$Cl^*O_2-HClO_2$	25	0·000548 *f* $KClO_2$, 0·000164 *f* ClO_2, 0·5 *f* $HClO_4$	ClO_2 in CCl_4	~6 s.	24
^{38}Cl (38 m.)	$Cl^*O_2-ClO_2^-$	25	0·00545 *f* $KClO_2$, 0·000109 *f* ClO_2, *p*H ~5.	ClO_2 in CCl_4	~6 s.	24
^{38}Cl (38 m.)	$Cl^*O_2-ClO_3^-$	25	0·0414 *f* ClO_2, 0·05 *f* $KClO_3$, 0·05 *f* $HClO_4$ or *p*H 7·2.	ClO_2 in CCl_4	>3 h.	24
^{38}Cl (38 m.)	$ClO_2^- - Cl^{*-}$, Cl^*O^-	25	0·048 *f* ClO_2^-, 0·017 *f* ClO^-, 0·017 *f* Cl^-, 0·1 *f* OH^-.	Soln. acidified, ClO_2 formed in CCl_4 (Cl_2 ext. from CCl_4 by Cl^-, $HPO_4^=$)	*7 ± 2·5 h.*	25
^{38}Cl (38 m.)	$ClO_3^- - Cl_2^*$	25	0·75 *f* $NaClO_3$, 0·015 *f* Cl_2, 4·5 *f* H_2SO_4.	Cl_2 in CCl_4	*>18 h.*	25
^{38}Cl (38 m.)	$ClO_3^- - Cl_2^*$	93	1·0 *f* $NaClO_3$, 0·026 *f* Cl_2, 3·0 *f* H_2SO_4.	Cl_2 in CCl_4	*>4 h.*	25
^{38}Cl (38 m.)	$ClO_3^- - Cl_2^*$	Rm.	1·0 *f* $NaClO_3$, 0·01 *f* Cl_2, 0·5 *f* H_2SO_4.	AgCl(s)	90 m.	108
^{35}Cl (stable)	$AsCl_3-HCl^*$	60	....	....	Very short	109
^{38}Cl (38 m.)	$PCl_3-Cl_2^*$	23	0·0421 *f* PCl_3, 0·0589 *f* Cl_2 in dry CCl_4.	Cl_2(g) or Hg_2Cl_2(s)	<70 s.	84
^{35}Cl (stable)	PCl_3-HCl^*	Rm.	....	....	Very short	109
^{38}Cl (38 m.)	$PCl_5-Cl_2^*$	23	0·0276 *f* PCl_5, 0·0295 *f* Cl_2 in dry CCl_4.	Cl_2(g) or Hg_2Cl_2(s)	<40 s.	84
^{35}Cl (stable)	$POCl_3-HCl^*$	...	....	....	Long	109
^{35}Cl (stable)	$S_2Cl_2-HCl^*$	60	....	....	Very long	109
^{35}Cl (stable)	$SiCl_4-HCl^*$	60	....	....	Very long	109

† Data corrected (C. B. A.)

Element and Tracer	Reactants	Temp. °C.	Other Conditions	Separation Method	Half-Time of Exchange	Lit. Ref.
^{38}Cl (38 m.)	1,2-$[Co(en)_2Cl_2]^+ - Cl^{*-}$	30	No isomerization	1,2-$[Co(en)_2Cl_2]NO_3(s)$	>6 h.	110
^{38}Cl (38 m.)	1,2-$[Co(en)_2(H_2O)Cl]^{++} - Cl^{*-}$	18	No isomerization	1,2-$[Co(en)_2(H_2O)Cl]SO_4(s)$	>4·5 h.	110
^{38}Cl (38 m.)	1,6-$[Co(en)_2Cl_2]^+ - Cl^{*-}$	60	No isomerization	1,6-$[Co(en)_2Cl_2]NO_3(s)$	>25 m.	110
^{38}Cl (38 m.)	1,6-$[Co(en)_2Cl_2]^+ - Cl^{*-}$	...	0·2 *f* 1,6-$[Co(en)_2Cl_2]Cl$, 0·14 *f* NaCl, under conditions leading to isomerization	Evap., ext. by ice water, HNO_3 added, 1,6-$[Co(en)_2(H_2O)Cl_2]NO_3(s)$ ppt.	<15 m.	110
^{38}Cl (38 m.)	$CCl_4 - Cl_2^*$	Rm.	Illuminated	Ext. by $SO_3^=$	>7 h.	111
^{35}Cl (stable)	$CCl_4 - HCl^*$	...	....	....	Very long	109
^{38}Cl (38 m.)	$CH_3COCl - AlCl_3^*$	50	5 g $AlCl_3$ in 3 g $CH_3COCl(l)$	$CH_3COCl(g)$	<60 s.	74
^{38}Cl (38 m.)	*tert*-$C_4H_9Cl - Cl^{*-}$	15	0·255 *f* C_4H_9Cl, 0·0256 *f* LiCl in dry HCOOH	C_4H_9Cl in ether and $Cl^-(aq)$	*4·1 ± 0·2 m.*	50
^{38}Cl (38 m.)	*tert*-$C_4H_9Cl - Cl^{*-}$	15	0·196 *f* C_4H_9Cl, 0·078 *f* LiCl in HCOOH, 10% water	C_4H_9Cl in ether and $Cl^-(aq)$	>14 h.	50
^{38}Cl (38 m.)	*tert*-$C_4H_9Cl - AlCl_3^*$	50	....	$C_4H_9Cl(g)$	<60 s.	74
^{38}Cl (38 m.)	*p*-$NO_2C_6H_4CH_2Cl - Cl^{*-}$	30·0	0·05771 *f* $NO_2C_6H_4CH_2Cl$, 0·01146 *f* LiCl in acetone, 10 vol. % H_2O	LiCl(aq) and $NO_2C_6H_4$-CH_2Cl in C_6H_6	*150 ± 10 h.*	112
^{38}Cl (38 m.)	*iso*Bornyl-chloride – HCl^*	20	0·300 *f* $C_{10}H_{17}Cl$, 0·084 *f* HCl in $CHCl_3$, $C_6H_5NO_2$	HCl(aq)	>3·5 h.	103
^{38}Cl (38 m.)	Camphene hydrochloride $- HCl^*$	20	0·158 *f* $C_{10}H_{17}Cl$, 0·075 *f* HCl in $CHCl_3$, $C_6H_5NO_2$	HCl(aq)	<135 s.	103
^{38}Cl (38 m.)	Camphene hydrochloride $- HCl^*$	0	0·158 *f* $C_{10}H_{17}Cl$, 0·158 *f* HCl in $CHCl_3$	HCl(aq)	27 m.	103

^{82}Br (34 h.)	$Br_2 - Br^{*-}$	Rm.	....	Br_2 in CCl_4	<15 s.	11
^{82}Br (34 h.)	$Br_2 - HBr^*$	Rm.	38·5 mm $Br_2(g)$, 69 mm $HBr(g)$	$Br_2(s)$	<30 s.	7,8
^{82}Br (34 h.)	$Br_2^* - HBr$	Rm.	In dry CCl_4	$Hg_2Br_2(s)$	<30 s.	6
^{82}Br (34 h.)	$Br^{*-}(aq) - Br^{*-}$ in organic solvent	~-30 to Rm.	$Br^-(aq) \cong Br^-(organic) = 0{\cdot}15-2\,f$	$AgBr(s)$	<15 s.	113
^{82}Br (34 h.) ^{80m}Br (4·4 h.)	$BrO_3^- - Br_2^*$	100	Neutral soln.	....	>110 d.	85
^{82}Br (34 h.)	$BrO_3^- - Br_2^*$	25·0	0·100 f $NaBrO_3$, 0·00059 f Br_2, 0·1006 f HNO_3	Br_2 in CCl_4	*220 ± 20 h.*	114
^{82}Br (34 h.)	$BrO_3^- - Br_2^*$	25·0	0·100 f $NaBrO_3$, 0·000259 f Br_2, 0·1006 f HNO_3	Br_2 in CCl_4	*390 ± 20 h.*	114
^{82}Br (34 h.)	$BrO_3^- - Br_2^*$	Rm.	1·13 f $NaBrO_3$, 0·012 f Br_2, 1·101 f HNO_3 or $HClO_4$	Br_2 in CCl_4	*40 m.*	108
^{80m}Br (4·4 h.)	$SeBr_4^* - Br_2^*$	45	In CS_2	$Br_2(g)$	<15 m.	115
^{82}Br (34 h.)	$PBr_3 - Br_2^*$	23	0·0309 f PBr_3, 0·0414 f Br_2 in dry CCl_4	$Br_2(g)$ or $Hg_2Br_2(s)$	<40 s.	84
^{82}Br (34 h.)	$AsBr_3 - Br_2^*$	25	In CCl_4	$Br_2(g)$	<150 s.	72
^{82}Br (34 h.)	$HgBr_2 - Br_2^*$	$\lesssim 0$	0·00167 f $HgBr_2$, 0·0063 f Br_2 in CS_2	$Br_2(g)$	<40 s.	116
^{82}Br (34 h.)	$SnBr_4 - Br_2^*$	25	In CCl_4	$Br_2(g)$	<150 s.	72
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$PtBr_4^= - Br^{*-}$	16	0·20 f K_2PtBr_4, 0·35 f KBr	$Pt(NH_3)_4-PtBr_4(s)$	10 m.	117,86
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$PtBr_6^= - Br^{*-}$	100	0·15 f K_2PtBr_6, 0·35 f KBr	$K_2PtBr_6(s)$	<30 m.	117,86
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$Pt(NH_3)_2Br_2^* - PtBr_4^=$	18	0·128 f $Pt(NH_3)_2Br_2$, 0·056 f K_2PtBr_4	$Pt(NH_3)_4-PtBr_4(s)$	<30 m.	117

Element and Tracer	Reactants	Temp. °C.	Other Conditions	Separation Method	Half-Time of Exchange	Lit. Ref.
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$CHBr_3-(AlBr_3{}^*)_n$	Rm.	....	$(AlBr_3)_n$ hydrolyzed	<4·5 m.	78,118
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$CHBr_3-C_2H_5Br^*$	$\leq$38	Catalyzed by $(AlBr_3)_n$	C_2H_5Br(g)	<10 m.	119,120
^{82}Br (34 h.)	$CBr_4-Br_2{}^*$	Rm.	Liquid phase	....	Long	69
^{82}Br (34 h.)	$CBr_4-Br_2{}^*$	107–160	Liquid phase	....	Meas.	69
^{82}Br (34 h.)	$CBr_4-Br_2{}^*$	170–200	Vapor phase	....	Meas.	69
^{82}Br (34 h.)	CBr_4-Br_2	95	In CCl_4, illuminated (4100–4500 A.)	....	....	121
^{82}Br (34 h.)	$CCl_3Br-Br_2{}^*$	Rm.	0·03 *f* Br_2 in CCl_3Br(l)	Br_2 ext. by I^-(aq)	>2400 h.	70
^{82}Br (34 h.)	$CCl_3Br-Br_2{}^*$	100	0·029 *f* Br_2 in CCl_3Br(l) (9·3*f*)	Br_2 ext. by I^-(aq)	~*6 h.*	70
^{82}Br (34 h.)	$CCl_3Br-Br_2{}^*$	125	0·028 *f* Br_2 in CCl_3Br(l) (9·0*f*)	Br_2 ext. by I^-(aq)	~*30 m.*	70
^{82}Br (34 h.)	$CCl_3Br-Br_2{}^*$	76	0·080 *f* CCl_3Br, 0·003 *f* Br_2 in CCl_4	Br_2 ext. by $NO_2{}^-$(aq)	>17 h.	72
^{82}Br (34 h.)	$CCl_3Br-Br_2{}^*$	76	0·080 *f* CCl_3Br, 0·003*f* Br_2 in CCl_4, illuminated (5000–6100 A.)	Br_2 ext. by $NO_2{}^-$(aq)	<5 m.	72
^{82}Br (34 h.)	$CCl_3Br-Br_2{}^*$	135	0·207 *f* CCl_3Br, 0·0028 *f* Br_2 in CCl_4	Br_2 ext. by I^-(aq)	~*3 h.*	70
^{82}Br (34 h.)	$CCl_3Br-Br_2{}^*$	170	0·194 *f* CCl_3Br, 0·00274 *f* Br_2 in CCl_4	Br_2 ext. by I^-(aq)	~*10 m.*	70
^{82}Br (34 h.)	$CCl_3Br-Br_2{}^*$	170	0·0042 *f* CCl_3Br(g), 0·00037 *f* Br_2(g)	Br_2 ext. by I^-(aq)	~*5 h.*	70

^{82}Br (34 h.)	$CCl_3Br^* - Br_2^*$	146	0·0335 f $CCl_3Br(g)$, 0·0034 f $Br_2(g)$	Br_2 ext. by $NO_2^-(aq)$	*18·7 h.*	32
^{82}Br (34 h.)	$CCl_3Br^* - Br_2^*$	183	0·0325 f $CCl_3Br(g)$, 0·0033 f Br(g)	Br_2 ext. by $NO_2^-(aq)$	*46·5 m.*	32
^{82}Br (34 h.)	$C_2H_5Br - Br_2^*$	Rm.	Vapor phase, illuminated	$Br_2(s)$	>125 h.	122
^{82}Br (34 h.)	$C_2H_5Br - Br_2^*$	>Rm.	Vapor phase	$Br_2(s)$	Meas.	122
^{82}Br (34 h.)	$C_2H_5Br - Br_2^*$	$\lesssim$350	Vapor phase	$Br_2(s)$	>13 h.	123
^{82}Br (34 h.)	$C_2H_5Br - HBr^*$	Rm.	Vapor phase	$C_2H_5Br(s)$	>27 h.	122
^{82}Br (34 h.)	$C_2H_5Br - HBr^*$	200	0·0069 f $C_2H_5Br(g)$, 0·53 f HBr(g), small surface to vol. ratio	$C_2H_5Br(s)$	>67 h.	123
^{80m}Br (4·4 h.)	$C_2H_5Br - (AlBr_3^*)_n$	~15	....	$C_2H_5Br(g)$	1·5 m.	124
^{80m}Br (4·4 h.)	$C_2H_5Br - (AlBr_3^*)_n$	~15	With nitrobenzene added in 2:1 mole ratio to $AlBr_3$	$C_2H_5Br(g)$	350 m.	124
^{82}Br (34 h.), ^{80m}Br (4·4 h.), ^{80}Br (18 m.)	$C_2H_5Br - (AlBr_3^*)_n$	Rm.	In CS_2	$(AlBr_3)_n$ hydrolyzed	<15 s.	79,125
^{80m}Br (4·4 h.)	$C_2H_5Br - SnBr_4^*$	~15	....	$C_2H_5Br(g)$	>27 h.	124
^{82}Br (34 h.)	$CH_2BrCH_2Br - Br_2^*$	100	28 mole % $C_2H_4Br_2$, 24 mole % Br_2, 48 mole % CCl_4	Br_2 ext. by $NO_2^-(aq)$	>20 h.	72
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$CH_2BrCH_2Br - (AlBr_3^*)_n$	Rm.	Liquid phase	$(AlBr_3)_n$ hydrolyzed	<4·5 m.	78,118
^{80m}Br (4·4 h.)	$CH_2BrCH_2Br - SbBr_3^*$	132	Liquid phase (?)	$SbBr_3$ hydrolyzed	6 h.	124
^{82}Br (34 h.), ^{80m}Br (4·4 h.), ^{80}Br (18 m.)	$CH_2Br^*CH_2Br^* - C_2H_5Br^*$	$\lesssim$38	6·0 ml $C_2H_5Br(l)$, 4·5 ml $C_2H_5Br_2(l)$	$C_2H_5Br(g)$	>10 h.	119,120

Element and Tracer	Reactants	Temp. °C.	Other Conditions	Separation Method	Half-Time of Exchange	Lit. Ref.
^{82}Br (34 h.), ^{80m}Br (4·4 h.), ^{80}Br (18 m.)	$CH_2Br^*CH_2Br^*$ – $C_2H_5Br^*$	≲38	7·0 ml $C_2H_5Br(l)$, 5·0 ml $C_2H_4Br_2(l)$, 0·28 g $(AlBr_3)_n$	$C_2H_5Br(g)$	<10 m.	119,12?
^{80m}Br (4·4 h.)	$CH_2{=}CHBr$ – $(AlBr_3{}^*)_n$	0	Minimum polymerization	$C_2H_3Br(g)$	<30 s.	124
^{80m}Br (4·4 h.)	CH_3COBr – $SnBr_4{}^*$	~15	. . . .	$CH_3COBr(g)$	18 m.	124
^{82}Br (34 h.)	$CH_3CH_2CH_2Br$ – Br^{*-}	25·1	0·1244 *f* C_3H_7Br, 0·0375 *f* LiBr in acetone, 10 vol. % H_2O	$Br^-(aq)$ and C_3H_7Br in C_6H_6	*33·1 ± 1·7 h.*	41
^{82}Br (34 h.)	$CH_3CHBrCH_3$ – Br^{*-}	25·1	0·1504 *f* C_3H_7Br, 0·0433 *f* LiBr in acetone, 10 vol. % H_2O	$Br^-(aq)$ and C_3H_7Br in C_6H_6	*810 ± 40 h.*	41
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$CH_2BrCH_2CH_2Br$ – $(AlBr_3{}^*)_n$	Rm.	. . . .	$(AlBr_3)_n$ hydrolyzed	<4·5 m.	78,118
^{82}Br (34 h.)	$CH_3CHBrCOOH$ – Br^{*-}	22	0·333 *f* $CH_3CHBrCOOH$, 0·333 *f* LiBr in acetone	OH^- added, evap., acidified, $CH_3CHBrCOOH$ in ether	*33·7 ± 1·0 m.*	47
^{82}Br (34 h.)	$CH_3CHBrCOOH$ – Br^{*-}	100	Non-equilibrium, initially: 0·0346 *f* NaBr, 0·0270 *f* $CH_3CHBrCOOH$ ($t_{1/2}$ is for exchange in the absence of hydrolysis)	$CH_3CHBrCOOH$ in ether	*27 m.*	126
^{80m}Br (4·4 h.)	$CH_2{=}CHCH_2Br$ – $(AlBr_3{}^*)_n$	~15	5% soln. in CS_2	$(AlBr_3)_n$ hydrolyzed	<45 s.	124
^{80m}Br (4·4 h.)	$CH_2{=}CHCH_2Br$ – $SnBr_4{}^*$	~15	. . . .	$C_3H_5Br(g)$	>7 h.	124
^{82}Br (34 h.)	*n*-$C_4H_9Br^*$ – Br^{*-}	24·4	0·25 *f* C_4H_9Br, 0·10 *f* LiBr in acetone, 10 vol. % H_2O	$Br^-(aq)$ and C_4H_9Br in C_6H_6	*23·9 ± 1·3 h.*	42
^{82}Br (34 h.)	*n*-C_4H_9Br – Br^{*-}	59·6	0·905 *f* C_4H_9Br, 0·037 *f* LiBr in acetone, 10 vol. % H_2O	$Br^-(aq)$ and C_4H_9Br in C_6H_6	*120 ± 5 m.*	42
^{82}Br (34 h.)	*n*-C_4H_9Br – Br^{*-}	25·0	0·0993 *f* C_4H_9Br, 0·0119 *f* LiBr in dry acetone	$Br^-(aq)$ and C_4H_9Br in C_6H_6	*96 ± 3 m.*	43

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^{82}Br (34 h.)	*n*-$C_4H_9Br-Br^{*-}$	26	0·045 *f* C_4H_9Br, 0·019 *f* LiBr in dry acetone	C_4H_9Br(g)	170 m.	127,128
^{82}Br (34 h.)	*n*-$C_4H_9Br-Br^{*-}$	26	0·045 *f* C_4H_9Br, 5 × 10^{-5} *f* LiBr in dry acetone	C_4H_9Br(g)	60 m.	127,128
^{82}Br (34 h.)	*n*-$C_4H_9Br-Br^{*-}$	25·0	0·100 *f* C_4H_9Br, 0·055 *f* LiBr in ethylene glycol diacetate	Br^-(aq) and C_4H_9Br in C_6H_6	113 h.	43
^{82}Br (34 h.)	*iso*-$C_4H_9Br-Br^{*-}$	24·9	0·1163 *f* C_4H_9Br, 0·0501 *f* LiBr in acetone, 10 vol. % H_2O	Br^-(aq) and C_4H_9Br in C_6H_6	*830 ± 50 h.*	41
^{82}Br (34 h.)	*tert*-$C_4H_9Br-Br^{*-}$	100	0·079 *f* C_4H_9Br, 0·033 *f* LiBr in ethylene glycol diacetate	Br^-(aq)	48 m.	43
^{80m}Br (4·4 h.)	*tert*-$C_4H_9Br^*-(AuBr_3)_n$	~ 15	In ether	C_4H_9Br(g)	15 m.	124
^{82}Br (34 h.)	$CH_3CH_2{=}CBrCH_3-Br^{*-}$	30	In acetone, no isomerization	. . . .	Meas.	129
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	*iso*-$C_5H_{11}Br-(AlBr_3{}^*)_n$	Rm.	. . . .	$(AlBr_3)_n$ hydrolyzed	<4·5 m.	78,118
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	*iso*-$C_5H_{11}Br-C_2H_5Br^*$	$\lesssim$38	Catalyzed by $(AlBr_3)_n$	C_2H_5Br(g)	<15 m.	119,120
^{82}Br (34 h.)	*sec*-octyl bromide-Br^{*-}	65·5	0·045 *f* $C_8H_{17}Br$, 2·6 × 10^{-4} *f* LiBr in dry acetone	$C_8H_{17}Br$(g)	36 m.	127
^{82}Br (34 h.)	*sec*-octyl bromide-Br^{*-}	65·5	0·045 *f* $C_8H_{17}Br$, 0·039 *f* LiBr in dry acetone	$C_8H_{17}Br$(g)	120 m.	127
^{82}Br (34 h.)	$C_6H_5Br-NaBr^*$	Rm.	. . . .	Br^-(aq)	>30 m.	78,118
^{82}Br (34 h.)	$C_6H_5Br-LiBr^*$	158	0·22 *f* C_6H_5Br, 0·22 *f* LiBr in di-ethylene glycol	. . . .	>13 h.	130
^{82}Br (34 h.)	$C_6H_5Br-CuBr_2{}^*$	16	0·2 *f* C_6H_5Br, 0·1 *f* $CuBr_2$ in 95% ethanol	. . . .	>7 h.	81

Element and Tracer	Reactants	Temp. °C.	Other Conditions	Separation Method	Half-Time of Exchange	Lit. Ref.
^{82}Br (34 h.)	$C_6H_5Br-SbBr_3^*$	155	0·7 *f* $SbBr_3$ in $C_6H_5Br(l)$	....	>50 h.	81
^{80m}Br (4·4 h.)	$C_6H_5Br-(AlBr_3^*)_n$	~15	....	$C_6H_5Br(g)$	20 h.	124
^{80m}Br (4·4 h.)	$C_6H_5Br-(AlBr_3^*)_n$	100	....	$C_6H_5Br(g)$	36 m.	124
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	*p*-$C_6H_4Br_2-(AlBr_3^*)_n$	Rm.	....	$(AlBr_3)_n$ hydrolyzed	~50 m.	78, 118
^{80m}Br (4·4 h.)	$C_6H_5CH_2Br-SnBr_4^*$	~15	....	$C_6H_5CH_2Br(g)$	<40 m.	124
^{82}Br (34 h.)	*p*-$NO_2C_6H_4CH_2Br-Br^{*-}$	30·0	0·0106 *f* $NO_2C_6H_4$-CH_2Br, 0·0290 *f* LiBr in acetone, 10 vol. % H_2O	Br^-(aq) and $NO_2C_6H_4CH_2Br$ in C_6H_6	*8·1 ± 0·3 m.*	112
^{82}Br (34 h.)	$C_6H_5CHBrCH_3-Br^{*-}$	30·2	0·20 *f* C_6H_5CHBr-CH_3, 0·20 *f* LiBr in dry acetone	Br^-(aq) and $C_6H_5CHBrCH_3(s)$	*33 ± 4 m.*	46
^{82}Br (34 h.)	ω-bromostyrene – LiBr*	216	0·21 *f* bromostyrene, 0·21 *f* LiBr in diethylene glycol	....	17 h.	130
^{82}Br (34 h.)	triphenylbromoethylene – LiBr*	216	0·18 *f* triphenylbromoethylene, 0·18 *f* LiBr in diethylene glycol	....	4·5 h.	130
^{82}Br (34 h.)	*o*-bromonitrobenzene – LiBr*	216	0·21 *f* bromonitrobenzene, 0·21 *f* LiBr in diethylene glycol	....	46 h.	130
^{82}Br (34 h.)	2,4-dinitrobromobenzene – Br^{*-}	100	0·0766 *f* $C_6H_3(NO_2)_2$-Br, 0·0577 *f* LiBr in ethylene glycol diacetate	Br^-(aq) and $C_6H_3(NO_2)_2Br$ in C_6H_6	*62·6 ± 3·3 h.*	43
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	α-$C_{10}H_7Br-(AlBr_3^*)_n$	Rm.	In α-$C_{10}H_7Br(l)$	$(AlBr_3)_n$ hydrolyzed	~50 m.	78, 118
^{82}Br (34 h.)	α-bromonaphthalene – LiBr*	216	0·21 *f* $C_{10}H_7Br$, 0·21 *f* LiBr in diethylene glycol	....	17 h.	130

^{82}Br (34 h.)	α-bromonaphthalene – LiBr*	242	0·21 *f* $C_{10}H_7Br$, 0·21 *f* LiBr in diethylene glycol	. . . .	2·1 h.	130
^{82}Br (34 h.)	α-bromonaphthalene – LiBr*	240	0·21 *f* $C_{10}H_7Br$, 0·21 *f* LiBr in triethylene glycol	. . . .	21 h.	130
^{82}Br (34 h.)	α-bromonaphthalene – LiBr*	260	0·21 *f* $C_{10}H_7Br$, 0·21 *f* LiBr in triethylene glycol	. . . .	7 h.	130
^{82}Br (34 h.)	α-bromonaphthalene – $CuBr_2$*	200	0·2 *f* $C_{10}H_7Br$, 0·1 *f* $CuBr_2$, in quinoline	. . . .	>7 h.	81
^{82}Br (34 h.)	α-bromonaphthalene – $(AlBr_3{}^*)_n$	75	1·2 *f* $C_{10}H_7Br$, 0·14 *f* $AlBr_3$, in benzene	. . . .	>13 h.	81
^{82}Br (34 h.)	β-bromonaphthalene – LiBr*	216	0·21 *f* $C_{10}H_7Br$, 0·21 *f* LiBr in diethylene glycol	. . . .	1·1 h.	130
^{82}Br (34 h.)	β-bromonaphthalene – LiBr*	240	0·21 *f* $C_{10}H_7Br$, 0·21 *f* LiBr in triethylene glycol	. . . .	1·9 h.	130
^{82}Br (34 h.)	9-bromoanthracene – LiBr*	240	0·21 *f* $C_{14}H_9Br$, 0·21 *f* LiBr in triethylene glycol	. . . .	18 h.	130
^{82}Br (34 h.)	9-bromoanthracene – LiBr*	260	0·21 *f* $C_{14}H_9Br$, 0·21 *f* LiBr in triethylene glycol	. . . .	5·1 h.	130
^{82}Br (34 h.)	9,10-dibromoanthracene – LiBr*	242	0·10 *f* $C_{14}H_8Br_2$, 0·20 *f* LiBr in triethylene glycol	. . . .	11 h.	130
^{128}I (25·0 m.)	$I_2{}^* - I^{*-}$	Rm.	. . . .	I_2 in ether	*<15 s.*	18, 12
^{128}I (25·0 m.)	$I_2 - HI^*$	Rm.	In vapor phase	$I_2(s)$	<30 s.	7
^{128}I (25·0 m.)	$I_2 - HI^*$	Rm.	In dry pentane	. . . .	<30 s.	7
^{128}I (25·0 m.)	$I^{*-}(aq) - I^{*-}$ in C_2H_5OH	-31	5 ml 0·3 *f* KI(aq), 25 ml 0·3 *f* KI in C_2H_5OH	AgI(s)	<15 s.	113
^{131}I (8·0 d.)	$IO_3{}^- - I^{*-}$	50·0	Neutral soln.	Acidified, I_2 in C_6H_6	*>30 y.*	20

Element and Tracer	Reactants	Temp. °C.	Other Conditions	Separation Method	Half-Time of Exchange	Lit. Ref.
I	$IO_3^- - I^{*-}$	200	0·143 *f* KIO_3, 0·13 *f* KI	....	38 h.	19
I	$IO_3^- - I^{*-}$	250	0·143 *f* KIO_3, 0·13 *f* KI	....	100 m.	19
I	$IO_3^- - I^{*-}$	300	0·143 *f* KIO_3, 0·13 *f* KI	....	6 m.	19
^{131}I (8·0 d.)	$IO_3^- - I_2^*$	25·0	0·099 *f* HIO_3, 7×10^{-4} *f* I_2	I_2 in $CHCl_3$ or CCl_4	*280 ± 4 h.*	20
^{131}I (8·0 d.)	$IO_3^- - I_2^*$	50·0	0·099 *f* HIO_3, 7×10^{-4} *f* I_2	I_2 in CCl_4	*22·4 ± 0·6 h.*	20
^{131}I (8·0 d.)	$IO_3^- - I_2^*$	25·0	0·020 *f* HIO_3, 5×10^{-4} *f* I_2, 0·99 *f* $HClO_4$	I_2 in C_6H_6	*159 + 5 h.*	20
^{131}I (8·0 d.)	$IO_3^- - I_2^*$	25·0	0·020 *f* $NaIO_3$, 0·00067 *f* I_2, 1·00 *f* $HClO_4$	I_2 in CCl_4	*208 h.*	131
^{131}I (8·0 d.)	$IO_3^- - I_2^*$	25·0	0·010 *f* $NaIO_3$, 0·001 *f* I_2, 1·5 *f* H_2SO_4	I_2 in $CHCl_3$	*216 ± 8 h.*	132
^{131}I (8·0 d.)	$IO_4^- - I^*O_3^-$	18(?)	0·03 *f* $NaIO_4$, 0·03 *f* $NaIO_3$, 0·02 *f* HNO_3	$Zn(IO_4)_2$(s), ppt. hot	150 h.	22
^{131}I (8·0 d.)	$IO_4^- - I^*O_3^-$	20(?)	0·03 *f* $NaIO_4$, 0·03 *f* $NaIO_3$, 0·02 *f* HNO_3, few mg I_2	$Zn(IO_4)_2$(s), ppt. hot	3 h.(?)	22
^{128}I (25·0 m.)	$SbI_3^* - I_2$	37	In dry pentane	....	<5 m.	133
^{128}I (25·0 m.)	$BiI_4^- - I^{*-}$	Rm.	....	BiI_3(s)	<30 s.	134
^{131}I (8·0 d.)	$BiI_4^{*-} - I^-$	Rm.	....	....	<30 s.	135
^{128}I (25·0 m.)	$PbI_4^{=} - I^{*-}$	Rm.	....	PbI_2(s)	<30 s.	134
^{128}I (25·0 m.)	$HgI_2^* - I^{*-}$	Rm.	....	AgI(s)	<2·5 m.	85
^{131}I (8·0 d.)	$HgI_4^{*=} - I^-$	Rm.	0·0005 *f* K_2HgI_4, 0·3 *f* KI	HgI_2 ppt. by addition of I_2 in CCl_4	<30 s.	135

^{128}I (25·0 m.)	$HgI_4^{*=}-I^{*-}$	100	....	AgI(s)	<2·5 m.	85
^{128}I (25·0 m.)	$TeI_6^{=}-I^{*-}$	Rm.	....	....	<30 s.	136
^{128}I (25·0 m.)	CH_3I-I^{*-}	Rm.	2·0 *f* CH_3I, 0·5 *f* NaI in 95% ethanol	AgI(s)	<1 m.	12,59
^{128}I (25·0 m.)	$CH_3I^*-I_2^*$	Rm.	In CH_3I or ether or ethanol or CCl_4 or CS_2	AgI(s)	>30 m.	59
^{128}I (25·0 m.)	$CH_3I-I_2^*$	100	In ethanol	AgI(s)	<3·5 m.	59
^{128}I (25·0 m.)	$CH_2I_2-I^{*-}$	Rm.	In ethanol	I^-(aq)(?)	>15 m.	59,12
^{128}I (25·0 m.)	$CH_2I_2-I^{*-}$	60	0·48 *f* CH_2I_2, 0·06 *f* NaI in dry ethanol	I^-(aq) and CH_2I_2 in ether	*20·6 ± 0·6 m.*	38
^{128}I (25·0 m.)	$CH_2I_2-I^{*-}$	100	In ethanol	I^-(aq)(?)	<30 s.	59
^{128}I (25·0 m.)	CHI_3-I^{*-}	Rm.	In ethanol	I^-(aq)(?)	>15 m.	59,12,18
^{128}I (25·0 m.)	CHI_3-I^{*-}	100	In ethanol	I^-(aq)(?)	<30 s.	59
^{128}I (25·0 m.)	$CHI_3-I_2^*$	Rm.	In ether	....	>3·5 h.	18
^{128}I (25·0 m.)	$C_2H_5I-I^{*-}$	24	10^{-4} mole C_2H_5I, 5 × 10^{-4} mole NaI in ethanol	I^-(aq) and C_2H_5I in ether	>70 m.	137
^{128}I (25·0 m.)	$C_2H_5I-I^{*-}$	100	10^{-4} mole C_2H_5I, 5 × 10^{-4} mole NaI in ethanol	I^-(aq) and C_2H_5I in ether	<15 s.	137
^{128}I (25·0 m.)	$C_2H_5I-I^{*-}$	25	0·91 *f* C_2H_5I, 0·135 *f* NaI in dry ethanol	I^-(aq) and C_2H_5I in ether	*63·5 ±3 m.*	38
^{128}I (25·0 m.)	$C_2H_5I-I^{*-}$	50	0·0199 *f* C_2H_5I, 0·0174 *f* NaI in ethanol	C_2H_5I(g)	*100 ± 2 m.*	39
^{128}I (25·0 m.)	$C_2H_5I-I^{*-}$	70·1	0·0199 *f* C_2H_5I, 0·0174 *f* NaI in ethanol	C_2H_5I(g)	*16·0 ± 0·3 m.*	39

Element and Tracer	Reactants	Temp. °C.	Other Conditions	Separation Method	Half-Time of Exchange	Lit. Ref.
^{131}I (8·0 d.)	$C_2H_5I-I^{*-}$	25	0·044 f C_2H_5I, 2·5 × 10^{-4} f NaI in methanol	$C_2H_5I(g)$	53 h.	127, 128
^{131}I (8·0 d.)	$C_2H_5I-I^{*-}$	25	0·044 f C_2H_5I, 4·3 × 10^{-4} f NaI, 0·059 f NH_4ClO_4 in methanol	$C_2H_5I(g)$	52·6 h.	127
^{131}I (8·0 d.)	$C_2H_5I-I^{*-}$	25	0·044 f C_2H_5I, 6·7 × 10^{-3} f NaI in methanol	$C_2H_5I(g)$	48 h.	127, 128
^{131}I (8·0 d.)	$C_2H_5I-I_2^*$	Rm.	0·04 f C_2H_5I, 0·002 f I_2 in hexane, dark	I_2 ext. by $SO_3^=$	>480 d.	61
^{131}I (8·0 d.)	$C_2H_5I-I_2^*$	Rm.	0·04 f C_2H_5I, 0·002 f I_2 in hexane, illuminated by W lamp	I_2 ext. by $SO_3^=$	>3·5 d. <480 d.	61
^{128}I (25·0 m.)	$C_2H_5I-I_2^*$	15	4 × 10^{-5} f I_2 in $C_2H_5I(l)$	I_2 ext. by $HSO_3^- + I^-$	~800 m.	138
^{128}I (25·0 m.)	$C_2H_5I-I_2^*$	55	4 × 10^{-5} f I_2 in $C_2H_5I(l)$	I_2 ext. by $HSO_3^- + I^-$	~170 m.	138
^{128}I (25·0 m.)	$C_2H_5I-I_2^*$	87	. . . .	I_2 in ether	>3·5 h.	18
^{128}I (25·0 m.)	$C_2H_5I-I^*$(?)	17	Exchange with iodine species produced in bombardment	Inorganic iodine ext. by KI(aq)	~260 m.	138
^{128}I (25·0 m.)	$C_2H_5I-I^*$(?)	55	Exchange with iodine species produced in bombardment	Inorganic iodine ext. by KI(aq)	~4 m.	138
^{131}I (8·0 d.)	*trans*-CHI = CHI – I_2^*	Rm.	0·04 f $C_2H_2I_2$, 0·002 f I_2 in hexane, dark	I_2 ext. by $SO_3^=$	>480 d.	61
^{131}I (8·0 d.)	*trans*-CHI = CHI – I_2^*	Rm.	0·04 f $C_2H_2I_2$, 0·002 f I_2, in hexane, illuminated by W lamp	I_2 ext. by $SO_3^=$	~50 m.	61
^{131}I (8·0 d.)	*trans*-CHI = CHI – I_2^*	25	0·012 f $C_2H_2I_2$, 0·0026 f I_2, in hexane, illuminated by W lamp	I_2 ext. by $SO_3^=$	26 m.	60

^{131}I (8·0 d.)	*trans*-CHI = CHI−I*	99·8	0·012 *f* $C_2H_4I_2$, 0·0026 *f* I_2 in decalin, dark	I_2 ext. by $SO_3^=$	12·6 h.	60
^{131}I (8·0 d.)	*cis*-CHI = CHI−I_2^*	99·8	0·012 *f* $C_2H_4I_2$, 0·0026 *f* I_2 in decalin, dark	I_2 ext. by $SO_3^=$	9·6 h.	60
^{131}I (8·0 d.)	$CH_2ICH_2I-I_2^*$	25	0·07 *f* $C_2H_4I_2$, 0·00088 *f* I_2 in CCl_4, dark	$Hg_2I_2(s)$	>350 h.	139
^{131}I (8·0 d.)	$CH_2ICH_2I-I_2^*$	100	0·07 *f* $C_2H_4I_2$, 0·00264 *f* I_2 in CCl_4, dark	$Hg_2I_2(s)$	120 h.	139
^{131}I (8·0 d.)	$CH_2ICH_2I-I_2^*$	25	0·07 *f* $C_2H_4I_2$, 0·00511 *f* I_2 in CCl_4, illuminated at 3130 A.	$Hg_2I_2(s)$	114 h.	139
^{131}I (8·0 d.)	$CH_2ICH_2I-I_2^*$	100	0·07 *f* $C_2H_4I_2$, 0·00198 *f* I_2 in CCl_4, illuminated at 3130 A.	$Hg_2I_2(s)$	28 h.	139
^{128}I (25·0 m.)	$CH_2ICOOH-I^{*-}$	Rm.	In H_2O	Na_2SO_4 added, CH_2ICOOH in ether	<30 s.	59
^{128}I (25·0 m.)	$CH_3CH_2CH_2I-I^{*-}$	35	0·75 *f* C_3H_7I, 0·135 *f* NaI in ethanol	I^-(aq) and C_3H_7I in ether	*35 ± 1 m.*	38
^{128}I (25·0 m.)	$CH_3CH_2CH_2I-I^{*-}$	49·8	0·01976 *f* C_3H_7I, 0·01635 *f* NaI in ethanol	$C_3H_7I(g)$	*164 ± 3m.*	39
^{128}I (25·0 m.)	$CH_3CH_2CH_2I-I^{*-}$	70·1	0·01959 *f* C_3H_7I, 0·01733 *f* NaI in ethanol	$C_3H_7I(g)$	*24·5 ± 4 m.*	39
^{128}I (25·0 m.)	$CH_3CHICH_3-I^{*-}$	50	1·62 *f* C_3H_7I, 0·142 *f* NaI in ethanol	I^-(aq) and C_3H_7I in ether	*66 ± 3 m.*	38
^{128}I (25·0 m.)	$CH_3CHICH_3-I^{*-}$	60·0	0·01988 *f* C_3H_7I, 0·01742 *f* NaI in ethanol	$C_3H_7I(g)$	*16·3 ± 0·2 h.*	39
^{128}I (25·0 m.)	$CH_3CHICH_3-I^{*-}$	70·1	0·01988 *f* C_3H_7I, 0·01661 *f* NaI in ethanol	$C_3H_7I(g)$	*5·7~~0 ± 0~~·5 h.*	39
^{128}I (25·0 m.)	$CH_2ICH_2COOH-I^{*-}$	Rm.	In H_2O	Na_2SO_4 added CH_2ICH_2COOH in ether	>15 m.	59

Element and Tracer	Reactants	Temp. °C.	Other Conditions	Separation Method	Half-Time of Exchange	Lit. Ref.
^{128}I (25·0 m.)	$CH_2ICH_2COOH - I^{*-}$	100	In H_2O	Na_2SO_4 added CH_2ICH_2-COOH in ether	<30 s.	59
^{131}I (8·0 d.)	$CH_2{=}CHCH_2I - I_2^*$	Rm.	0·04 *f* allyl iodide, 0·002 *f* I_2 in hexane, almost dark	I_2 ext. by $SO_3^=$	~50 s.	61
^{131}I (8·0 d.)	$CH_2{=}CHCH_2I - I_2^*$	Rm.	0·04 *f* allyl iodide, 0·002 *f* I_2 in hexane, room light	I_2 ext. by $SO_3^=$	~15 s.	61
^{128}I (25·0 m.)	$CH_2{=}CHCH_2I - I^{*-}$	Rm.	2·0 *f* C_3H_5I, 0·5 *f* NaI in 95% ethanol	AgI(s)	<1 m.	12,59
^{128}I (25·0 m.)	*n*-$C_4H_9I - I^{*-}$	50	0·64 *f* C_4H_9I, 0·135 *f* NaI in ethanol	I^-(aq) and C_4H_9I in ether	*14 ± 1 m.*	38
^{128}I (25·0 m.)	*iso*-$C_4H_9I - I^{*-}$	50	1·42 *f* C_4H_9I, 0·142 *f* NaI in ethanol	I^-(aq) and C_4H_9I in ether	*49 ± 5 m.*	38
^{128}I (25·0 m.)	*sec*-$C_4H_9I - I^{*-}$	50	1·42 *f* C_4H_9I, 0·142 *f* NaI in ethanol	I^-(aq) and C_4H_9I in ether	*61 ± 4 m.*	38
^{128}I (25·0 m.)	*tert*-$C_4H_9I - I^{*-}$	40	1·24 *f* C_4H_9I, 0·37 *f* NaI in ethanol	I^-(aq) and C_4H_9I in ether	*7·6 ± 0·6 m.*	38
^{128}I (25·0 m.)	*tert*-$C_4H_9I - I^{*-}$	0	0·2 *f* C_4H_9I, 0·01 *f* NaI in SO_2(l)	C_4H_9I(g)	3 m.	49
^{128}I (25·0 m.)	*tert*-$C_4H_9I - I^{*-}$	−38	0·2 *f* C_4H_9I, 0·01 *f* NaI in SO_2(l)	C_4H_9I(g)	15 m.	49
^{128}I (25·0 m.)	*n*-$C_5H_{11}I - I^{*-}$	50	0·56 *f* $C_5H_{11}I$, 0·135 *f* NaI in ethanol	I^-(aq) and $C_5H_{11}I$ in ether	*12·2 ± 0·2 m.*	38
^{128}I (25·0 m.)	*iso*-$C_5H_{11}I - I^{*-}$	50	0·715 *f* $C_5H_{11}I$, 0·137 *f* NaI in ethanol	I^-(aq) and $C_5H_{11}I$ in ether	*23·6 ± 1 m.*	38
^{128}I (25·0 m.)	*dl-sec*-octyl iodide$-I^{*-}$	30	0·1377 *f* $C_8H_{17}I$, 0·1706 *f* NaI in acetone	$C_8H_{17}I$ in CCl_4	*27·5 ± 2 m.*	45

^{128}I (25·0 m.)	$C_6H_5I-I^{*-}$	100	In ethanol	I^-(aq)(?)	>15 m.	59
^{131}I (8·0 d.)	$C_6H_5I-I_2^*$	Rm.	0·04 *f* C_6H_5I, 0·002 *f* I_2 in hexane, dark	I_2 ext. by $SO_3^=$	>480 d.	61
^{131}I (8·0 d.)	$C_6H_5I-I_2^*$	Pm.	0·04 *f* C_6H_5I, 0·002 *f* I_2 in hexane, illuminated by W lamp	I_2 ext. by $SO_3^=$	~ 1·7 d.	61
^{128}I (25·0 m.)	$C_6H_5CH_2I-I^{*-}$	0	0·2 *f* $C_6H_5CH_2I$, 0·019 *f* NaI in SO_2(l)	$C_6H_5CH_2I$(g)	5 m.(?)	49
^{128}I (25·0 m.)	*p*-$NO_2C_6H_4I-I^{*-}$	100	In ethanol	I^-(aq)(?)	>15 m.	59
^{128}I (25·0 m.)	*p*-$NH_2C_6H_4I-I^{*-}$	100	In ethanol	I^-(aq)(?)	>15 m.	59
^{128}I (25·0 m.)	*m*-$IC_6H_4COOH-I^{*-}$	Rm.	In acetone	I^-(aq)(?)	>15 m.	59
^{128}I (25·0 m.)	*p*-$IC_6H_4COOH-I^{*-}$	Rm.	In acetone	I^-(aq)(?)	>15 m.	59
^{131}I (8·0 d.)	2,6-diiodophenol $-I_2^*$	50	50% methanol	....	<20 m.	140
^{131}I (8·0 d.)	4,6-diiodophenol $-I_2^*$	50	50% methanol	....	<20 m.	140
^{131}I (8·0 d.)	2,4,6-triiodophenol $-I_2^*$	50	50% methanol	....	<20 m.	140
^{128}I (25·0 m.)	$[(C_6H_5)_2I]^+-I^{*-}$	78	In C_2H_5OH or 1:1 H_2O, C_2H_5OH	$[(C_6H_5)_2I]I$(s)	>4·5 h.	87
^{128}I (25·0 m.)	$[(C_6H_5)_2I]^+-I^{*-}$	105	1·5 g diphenyliodonium iodide in 6·0 ml C_6H_5I	$[(C_6H_5)_2I]I$(s)	>70 m.	87
^{128}I (25·0 m.)	Thyroxine $-I^{*-}$	38	....	AgI(s)	>7 h.	141
^{128}I (25·0 m.)	Diiodotyrosine(3,5) $-I^{*-}$	38	....	AgI(s)	>7 h.	141
^{131}I (8·0 d.)	Diiodotyrosine $-I^{*-}$	50	Aqueous solution, *p*H 5	....	<20 m.	140
^{131}I (8·0 d.)	Diiodotyrosine $-I_2^*$	50	Aqueous solution, *p*H 5	....	<20 m.	140

ISOTOPIC EXCHANGE REACTIONS - HETEROGENEOUS

Element and Tracer	Reactants	Temp. °C.	Other Conditions	Time	Extent of Exchange	Lit. Ref.
^{36}Cl (4·4 × 10^5 y.)	$AlCl_3(s) - CCl_4(l)$	-21	(The reaction appears to stop abruptly when the indicated % exchange has occurred)	. . .	15%	142
^{36}Cl (4·4 × 10^5 y.)	$AlCl_3(s) - CCl_4(l)$	25	(The reaction appears to stop abruptly when the indicated % exchange has occurred)	. . .	40%	142
^{36}Cl (4·4 × 10^5 y.)	$AlCl_3(s) - CCl_4(l)$	>75	. . . .	. . .	100%	142
^{38}Cl (38 m.)	$AgCl(s) - Cl^{*-}$	Rm.	AgCl(s) aged 1 y.	5 m.	~ 1 a.l.	143
^{38}Cl (38 m.)	$AgCl(s) - Cl^-$	Rm.	. . . .	2 m.	38 - 77%	135
^{80m}Br (4·4 h.), ^{80}Br (18 m.)	$Br_2(l) - Br^{*-}$	Rm. - 100	0·18 mole $Br_2(l)$; 100 ml 1 *f* NaBr: Br_2 vaporized on steam bath	30 m.	>75%	144
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$Al_2Br_6(s) - Br_2{}^*(g)$	Rm.	. . . .	10 m.	>95%	78, 118
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$Al_2Br_6(l) - Br_2{}^*(g)$	. . .	. . . .	10 m.	>95%	78, 118
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$Al_2Br_6(s) - HBr^*(g)$	Rm.	. . . .	10 m.	>95%	78, 118
^{82}Br (34 h.)	$Al_2Br_6(s) - CH_3Br^*(g)$	25	6·5 ml 70-mesh fused $AlBr_3(s)$; 298 mm $CH_3Br(g)$	33 m.	66%	80
^{80m}Br (4·4 h.)	$SbBr_3(s) - C_2H_5Br^*(l)$	~ 15	. . . .	100 m.	<5%	124
^{80m}Br (4·4 h.)	$SbBr_3(s) - CH_2Br^*CH_2Br^*(l)$	~ 15	. . . .	120 m.	<5%	124
^{80m}Br (4·4 h.)	$SbBr_3(s) -$ *tert*-$C_4H_9Br^*(l)$	~ 15	. . . .	30 m.	>95%	124
^{80m}Br (4·4 h.)	$AsBr_3(s) - C_2H_5Br(l)$	~ 15	. . . .	10 m.	<5%	124
^{82}Br (34 h.)	$BaBr_2(s) - CH_3Br^*(g)$	95	6·5 ml 70-mesh fused $BaBr_2(s)$; 368 mm $CH_3Br(g)$	160 m.	25%	80

^{80m}Br (4·4 h.)	$CuBr_2(s)-$*tert*-$C_4H_9Br^*(l)$	~15	....	60 m.	<5%	124
^{80m}Br (4·4 h.), ^{80}Br (18 m.)	$CuBr(s)-Br^{*-}$	Rm.	0·00135 mole CuBr, 10 ml 0·008 *f* NaBr	30 m.	8%	145
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$CuBr(s)-Br_2^*(l)$	<60	During bromination	<1 h.	~50%	82
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$CuBr_2^*(s)-Br_2^*(g)$	...	....	48 h.	~16%	82
^{80m}Br (4·4 h.)	$CuBr_2(s)-$*tert*-$C_4H_9Br^*(l)$	~15	....	90 m.	>1%	124
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$AuBr(s)-Br_2^*(l)$	<60	During bromination	<1 h.	~40%	82
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$AuBr_3(s)-Br_2^*(l)$	...	....	48 h.	~37%	82
^{80m}Br (4·4 h.)	$AuBr_3(s)-C_2H_5Br^*(l)$	~15	....	30 m.	>5%	124
^{80m}Br (4·4 h.)	$InBr_3(s)-C_2H_5Br^*(l)$	~15	....	30 m.	>1%	124
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$Hg_2Br_2^*(s)-HBr$ in CCl_4	Rm.	....	5 m.	<5%	6
^{80m}Br (4·4 h.)	$HgBr_2(s)-C_2H_5Br^*(l)$	~15	....	5 m.	<5%	124
^{80m}Br (4·4 h.)	$HgBr_2^*(s)-C_6H_5CH_2Br(l)$	~15	....	30 m.	>1%	124
^{80m}Br (4·4 h.)	$PBr_5(s)-C_2H_5Br^*(l)$	~15	....	120 m.	<5%	124
^{82}Br (34 h.)	$KBr(s)-CH_3Br^*(g)$	Rm.	....	...	<5%	80
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$AgBr^*(s)-Br^{*-}$	20	5·3 mmoles fresh AgBr(s); 5·9 mmoles KBr(aq)	1 m.	~10%	29
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$AgBr^*(s)-Br^{*-}$	20	5·3 mmoles fresh AgBr(s); 5·9 mmoles KBr(aq)	30 h.	>95%	29

Element and Tracer	Reactants	Temp. °C.	Other conditions	Time	Extent of Exchange	Lit. Ref.
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$AgBr^*(s) - Br^{*-}$	20	5·3 mmoles aged AgBr(s); 5·9 mmoles KBr(aq)	48 h.	~50%	29
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$AgBr^*(s) - Br^{*-}$	20	5·3 mmoles fused AgBr(s); 5·9 mmoles KBr(aq)	48 h.	<5%	29
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$AgBr(s) - Br^{*-}$	Rm.	Freshly coagulated AgBr(s); NaBr in H_2O, C_2H_5OH	3 m.	20%	30
^{82}Br (34 h.), ^{80m}Br (4·4 h.)	$AgBr(s) - Br^{*-}$	100	Aged AgBr(s)	30 m.	~50%	85
^{80m}Br (4·4 h.)	$AgBr(s) - Br^{*-}$	Rm.	0·5 mmole fresh AgBr; 20 ml 0·0015 *f* KBr	15 m.	86%	28
^{80m}Br (4·4 h.)	$AgBr(s) - Br^{*-}$	Rm.	0·5 mmole fresh AgBr; 20 ml 0·0015 *f* KBr	1 h.	98%	28
^{80m}Br (4·4 h.)	$AgBr(s) - Br^{*-}$	Rm.	10·6 mmoles aged AgBr; 14 ml 0·001 *f* KBr	1 h.	75%	28
^{80m}Br (4·4 h.)	$AgBr(s) - Br^{*-}$	Rm.	10·6 mmoles aged AgBr coated with Wool Violet; 14 ml 0·0008 *f* KBr	1 h.	24%	28
^{80}Br (34 h.)	$AgBr(s) - Br^{*-}$	~25	1·0 mmole fresh AgBr(s); 40 ml 0·005 *f* NaBr	5 m.	48%	33
^{80}Br (34 h.)	$AgBr(s) - Br^{*-}$	~25	1·0 mmole fresh AgBr(s); 40 ml 0·005 *f* NaBr	30 m.	90%	33
^{80}Br (34 h.)	$AgBr(s) - Br^{*-}$	~25	1·0 mmole fresh AgBr(s); coated with Methylene Blue: 40 ml 0·005 *f* NaBr	30 m.	20%	33
^{80}Br (34 h.)	AgBr(s) in gelatin – Br^{*-}	Rm.	0·76 mmole AgBr(s) in photographic plate; 100 ml 0·0076 *f* Br^-	31 h.	<5%	34
^{80m}Br (4·4 h.)	$AgBr(s) - Br_2^*$ in C_2H_5Br	Rm.	AgBr aged for various times in C_2H_5Br	70 m.	68 – 100%	31
^{80m}Br (4·4 h.)	$AgBr(s) - Br_2^*(g)$	Rm.	5·3 mmoles fresh air-dried AgBr(s), 0·55% surface	100 m.	64·2%	31
^{82}Br (34 h.)	$AgBr^*(s) - Br_2(g)$	160		Few h.	>95%	32

^{80}Br (34 h.)	$NaBrO_3(s) - CH_3Br^*(g)$	Rm.	. . . .	. . .	<5%	80
^{80m}Br (4·4 h.)	$ZnBr_2(s)$ − *tert*-$C_4H_3Br^*(l)$	~ 15	. . . .	90 m.	>1%	124
^{80m}Br (4·4 h.)	$C_6H_5Br(l) - Br^{*-}$	Rm.	. . . .	1 m.	<5%	146
^{128}I (25·0 m.)	$CuI(s) - I^{*-}$	Rm.	1·05 mmoles CuI(s); 10 ml 0·008 *f* NaI	30 m.	8%	145
^{128}I (25·0 m.)	$AgI^*(s) - I^-$	100	Freshly coagulated AgI(s)	30 m.	>95%	85
^{130}I (12·6 h.)	$AgI^*(s) - I^{*-}$	Rm.	Freshly coagulated AgI(s)	36 h.	~80%	147
^{130}I (12·6 h.)	$AgI^*(s) - I^{*-}$	Rm.	Aged AgI(s)	24 h.	~20%	147

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SECTION XLIII

USES OF THE RADIOHALOGENS OTHER THAN IN CHEMICAL STUDIES

By W. J. ARROL

Much work has been recorded on the use of radiohalogens in industrial research and in the fields of biochemistry and physiology and in diagnostic and therapeutic medicine. Early research with these nuclides was very uneven in quality, possibly because useful activities of radiohalogens of reasonable half-life were available before methods for their employment had been sufficiently systematized. This being so, a comprehensive survey would include much of doubtful value and it is preferable to select a few examples which serve to illustrate the utilization of the properties of the radiohalogens, dealing with these in order of ascending atomic weight.

BIOCHEMICAL AND PHYSIOLOGICAL APPLICATIONS OF RADIOHALOGENS

Fluorine-18 (see page 1004), the only fluorine isotope having a useful half-life, has been little applied in biochemical research. Injected intravenously as fluoride ion, it has been used to study the rate of its appearance in the saliva of cats under various conditions:[1] ^{18}F has also been used to study the distribution of radiofluoride in teeth and bone in cats and rats.[2]

Chlorine is of importance in both plants and animals, but because of the short half-life of ^{38}Cl and the long life and consequent low available specific activity of ^{36}Cl less has been done with it than with bromine and iodine in the field of biology. Most of the recorded studies concern the transport of chloride ion in various mammalian tissues.

Manery and Haege studied the penetration of interperitoneally and intravenously injected radiochloride solution into various tissues in rats and rabbits respectviely,[3] using ^{38}Cl (see page 1005) as a solution of lithium chloride. The ^{38}Cl$^-$ ion exchanged completely with the chloride in kidney, liver, muscles, cartilage and tendon in a few minutes after injection; the exchange was, however, far from complete in the testes even after one hour, and only a trace of radiochloride was found in brain tissue. Born and Timoféeff-Ressovsky[4] exposed mice to gaseous elementary chlorine labelled with ^{38}Cl: some were killed at once and others 5 and 8 minutes later. The results showed that if an animal was killed immediately after exposure, 79% of the total activity present was in the lungs, 9% in the kidneys and less in the liver and brain. At five minutes after exposure the lungs contained only 60% and the kidneys 24%, while at eight minutes the lung content had fallen to 45% and that of the kidneys had risen to 43%. The rise of activity in liver and brain was slow. From these and other accounts[5-7] it seems that chloride ion exchanges in a very few minutes between blood and many other tissues in living mammals, but that penetration into certain organs such as the brain is relatively very slow. In another similar experiment the time taken for the radiochloride concentration in the aqueous humour of the eye to reach half that of the blood plasma in a rabbit was found to be about 40 minutes.[8]

The penetration of chloride ion has also been studied in some isolated tissues with the aid of radioactive chlorine, for example with the red blood cells of the rabbit,[9] using ^{38}Cl as normal saline solution, prepared by a Szilard-Chalmers process on carbon tetrachloride as target material. Penetration of the erythrocytes was expected to be rapid, so normal saline solution labelled with ^{38}Cl was added at 0°C. to rabbit blood and the mixture shaken for only one minute and the blood then centrifuged. The active corpuscles were then mixed with inactive plasma and the active plasma with inactive corpuscles in order to prepare physically comparable sources for counting the ^{38}Cl. One gram of the corpuscles in the rabbit blood was found to contain about half as much ^{38}Cl as 1 g. of plasma, but as the ordinary chloride content of 1 g. of corpuscle of the rabbit is about 0·53 times that of 1 g. of plasma, the equilibration of radiochloride between plasma and corpuscles had reached completion at 0°C. in one minute plus the time taken in centrifuging the blood. The rate of penetration of corpuscles by chloride ion was, therefore, too fast to measure and was more than a hundred times as fast as that of phosphate ion labelled with ^{32}P.

The behaviour of ions in the tissues of living mammals is more complicated than considerations of overall transport through a membrane would suggest. Visscher *et al.*[10] point out that a membrane such as the intestine is a structure across which materials normally move in both directions and that studies of net transport give no information about the total rate of movement in either direction. They point out that only by the use of isotopically abnormal materials, whether radioactive or stable, can these absolute rates of movement be measured. In a long and careful study, these authors were able to make simultaneous measurements of the movement of water and of sodium or chloride ions between the intestines and the blood in dogs, by labelling the water with deuterium and the other ions with ^{24}Na and ^{38}Cl respectively. It was found, inter alia, that total directional rates and net transport rates predicted on the assumption that movement is due to diffusion differed from the experimentally determined values by as much as 200-fold. Normal osmosis could not cause the observed net movement of water between ileum and blood, nor could concentration gradients be the major cause of the observed chloride and sodium ion movements between the normal gut and the blood. The findings indicated a forced flow of fluid across the intestinal epithelium in both directions simultaneously, differences in the solute content of the water in the two streams and the relative rates of the streams determining the direction and magnitude of the net transport.

Ussing[11] studied the passage in both directions of sodium and chloride ion through isolated frog skin as a function of several different factors and observed the increase in the skin permeability in both directions in the presence of adrenaline and also the blocking effect of cyanide ion.

Bromine is not usually considered as taking part in mammalian metabolism. Up to about 1940 it was assumed that, in the body, administered chloride ion is rapidly distributed almost entirely throughout the extracellular phase. In experiments on the administration of large doses of inactive bromide to dogs and cats,[12] concentration ratios of chlorides in blood serum and in various tissues were compared with those for bromide in serum and in the same tissues and it was concluded that bromide was distributed similarly to chloride in all tissues except the brain. It was considered unlikely that any tissue was capable of concentrating bromine selectively, but in these experiments the thyroid glands were not examined.

Iodine is known to be selectively concentrated in thyroid tissue with remarkable efficiency and Perlman, Morton and Chaikoff, using radioactive bromine, re-examined the question whether bromine might concentrate in thyroid tissue.[13] Active bromine, ^{82}Br, prepared by the Szilard-Chalmers process on bromobenzene, was administered as very dilute aqueous solution. The authors estimated that one millicurie was contained in 10^{-9} g. of bromine: certainly the chemical dose of bromine containing 50 microcuries of ^{82}Br given to each animal was insufficient to disturb its metabolic processes in any way. The radiobromine solution was injected interperitoneally into rats and guinea pigs, and at intervals they were anæsthetized and killed. The radiobromine in various tissues was determined by adding carrier bromine as bromide and wet ashing with nitric acid after mashing the tissues with silver nitrate. The silver halides were filtered, mounted and their radioactivity determined. It was found that whereas in many tissues there was no evidence of concentration, thyroid tissue was able to take up bromine from serum, this effect being more marked in animals with hypertrophied thyroid glands produced by the administration of thyrotropic hormone. The whole effect was much less than with iodine, but it was definite and too large to be explained by simple diffusion of bromide ion from serum to thyroid tissue.

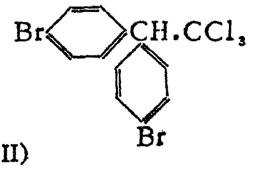
TRACING OF COMPOUNDS BY SUBSTITUTION OF RADIOACTIVE HALOGEN

Colloidal dyes, circulating in the blood, are known to concentrate in areas of increased permeability of the capillaries. It appeared possible that if such dyes were labelled with a γ-active nuclide such as ^{82}Br, they could be detected, say, in an area of inflammation and perhaps in tumours. This possibility was investigated with bromo-Evans blue[14-17] in dogs, rabbits and in tumour-bearing mice, though without significant results.

Before sex hormones labelled with carbon 14 had been synthesized, several efforts were made to label oestrogenically active materials with ^{82}Br for the study of the metabolism of the hormone. One such attempt involved the direct bromination of equilin to produce dibromo-oestrone:[18] the yield of dibromo-oestrone being 83%. It appeared in several animals that the mode of excretion was via the bile duct into the intestine and thence into the portal circulation and to the urine. Here, however, bromination had made a marked difference to the biological behaviour of oestrone, as dibromo-oestrone appeared to be but weakly oestrogenic, if indeed it was oestrogenic at all.

A synthetic hormone, 1,1-dimethyl-2-ethyl-2(6-methoxynaphthyl) propionic acid, can be brominated directly in carbon tetrachloride solution.[19] The bromine is substituted in the naphthalene nucleus and cannot be removed by exchange with bromide. Here again, bromine reduces the oestrogenic properties of the hormone and whereas the original oestrogen is physiologically active in the rat at a dose level of $1{\cdot}5 - 2\ \mu$g., the bromo-compound is active only at between 10 and 20 μg. In an earlier study, triphenylethylene, which is oestrogenic at the level of 10 g. in mice, was brominated and injected in olive oil solution into mice, the distribution with time being studied in male and female mice. In females, high concentrations appeared in ovaries, uterus and mammæ, but in the males the oestrogen concentrated only in the preputial glands.[20]

In all the foregoing experiments, bromine was substituted for hydrogen to produce a labelled compound. It is therefore not surprising that the brominated compound should have biological properties rather different from those of the original material. When a compound is made radioactive by substituting bromine for chlorine, however, much less alteration of its biological properties might be expected. In considering a possible label for the insecticide DDT, 1:1:1-trichloro-2:2-di(4-chlorophenyl)ethane (I), it was found that a bromine analogue (II) could readily be synthesized with ^{82}Br and had properties apparently identical with those of ordinary DDT except that the bromine analogue was slightly less toxic. Using this, preliminary studies were made on adult cockroaches and the larvæ of other insects to trace the insecticide after application.[21] Winteringham *et al.*[22-24] also using the bromine analogue of DDT, carried out an extensive investigation not only into the transport of the



(II)

activity inside insects, but also upon the compounds into which it is metabolized by insects and mammals and, further, upon the fate of DDT used to spray grain which would ultimately be eaten by animals and human beings.

The ^{82}Br was prepared by a Szilard-Chalmers reaction on bromobenzene in a pile irradiation and recovered as bromide, the enrichment factor being about 10. Synthesis of the DDT analogue was then carried out by the steps:-

$$Br^{*-} \rightarrow AgBr^{*} \rightarrow Br^{*}_2 \rightarrow C_6H_5Br^{*} \rightarrow (Br^{*}C_6H_4)_2CHCCl_3. \quad (II)$$

To separate, identify and measure the radioactive insecticide and its possible metabolites, a method of reversed-phase filter paper chromatography was developed and was made quantitative by cutting the strips of paper after the chromatogram was prepared and counting them, with a standard geometry, to find the position and amount of ^{82}Br in the various spots. DDT is known to lose hydrogen halide easily to give the corresponding ethylenic compound and in mammals to form a water soluble metabolite, $[(ClC_6H_4)_2CH.COO]^-$. The two compounds which might be metabolites of the bromine analogue of DDT would be $(BrC_6H_4)_2CCl_2$ (III), an ethylenic compound relatively non-toxic to insects, and $[(BrC_6H_4)_2CH.COO]^-$ (IV). When the chromatographic separation of mixtures of compounds (II), (III) and (IV) was carried out on the micromole scale, no exchange of bromine atoms was found to occur between these compounds during the analytical process. It was then shown that DDT-resistant houseflies could convert some compound (II) into compound (III) but not into compound (IV): mammals, on the other hand, metabolized a considerable proportion of (II) to (IV).

Iodine enters into animal metabolism and is a constituent of the hormone secreted by the thyroid gland. The availability of ^{131}I (see page 1007), of half life 8·0 days and emitting radiations which are quite easily measured, has facilitated much research on thyroid metabolism. Iodine 131 has also been used, like ^{82}Br, for labelling biological material by substitution.[25] As in the case of ^{82}Br labelling, this is not ideal, but it seems often to be justified if the iodine label is chemically stable and does not cause much change in the biological behaviour of the material.

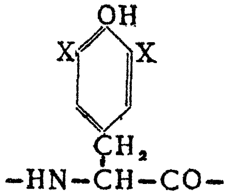
Insulin was labelled with iodine 131 to see whether the rate of removal of the material from the site of injection could be correlated with drop in blood sugar in an animal.[26] Insulin p-iodoazobenzene was prepared by making radioactive p-iodoaniline by the reaction:-

$$^{131}I_2 + C_6H_5NH_2 + NaHCO_3 \rightarrow {}^{131}I.C_6H_4NH_2 + Na^{131}I + H_2O + CO_2$$

afterwards diazotizing the p-iodoaniline and coupling the product with insulin. It was found in rabbits that blood sugar concentration varied inversely as the rate of absorption of the labelled insulin. With rats, it was found an hour after injection that the circulating blood contained a considerable fraction of the radioactivity and relatively large quantities were found in liver and kidneys. The deposition of activity in the latter sites might have been due to the splitting of the label from the insulin and does not by itself afford proof that insulin is deposited there intact. Similar work with insulin preparations, globin insulin and protamine zinc insulin, showed by direct observation of activity at the site of injection that the rates of absorption were in the order:

insulin, globin insulin (with zinc), protamine zinc insulin; and that the intensities of hypoglycaemic action could be correlated with these absorption rates.

It is possible to label proteins by substitution of halogens for hydrogen, almost certainly in the 3:5 positions X in the tyrosine residue of the protein.



Wormall[27] found that protein material could be halogenated and although its immunochemical properties were modified there was no reason to suspect extensive chemical decomposition. Fine and Seligman[28] wished to label plasma protein in dogs for the study of the apparent loss of plasma in traumatic shock. They had produced plasma protein labelled with ^{35}S biosynthetically by the administration of ^{35}S-labelled cystine and subsequent extraction of the biosynthesized ^{35}S-labelled plasma protein. This ^{35}S-labelled material would be chemically completely identical with normal protein. It was desirable to have a quicker and more convenient method of labelling the plasma protein and ^{82}Br was used. The rate of loss from the circulation of dogs of ^{82}Br-labelled plasma protein was compared with that of ^{35}S-labelled material, the latter being taken as normal. It was found that if the bromine content was not more than 0·04% of the protein brominated, the behaviour of the two labelled proteins was nearly identical. At higher levels of bromination, there was a progressively increased rate of loss of the brominated protein from plasma relative to the chemically and biologically normal ^{35}S-labelled material. Later, the same authors found it more convenient to use ^{131}I as label, because its decay scheme was suitable and, as higher specific activity ^{131}I was easily available, the proportion of halogen to protein was much lower.[29] This, too, proved to be a highly satisfactory labelled material for the purposes of the investigation in hand.

The labelling of antisera by substitution with ^{131}I has been carried out successfully.[30] The globulin molecule of an antiserum was iodinated and the mean number of iodine atoms per globulin molecule determined. Providing not more than 10 atoms of iodine per globulin molecule were introduced, there appeared to be no impairment of agglutinating power. Above that figure, as in the case already mentioned, modification of biochemical properties increased with increasing halogenation.

SYNTHETIC PLANT GROWTH REGULATORS

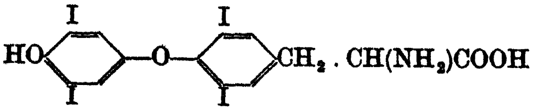
Several relatively simple chemical substances have the property of modifying the rate of growth of certain plants very markedly when applied to the leaves in low concentrations. One of these is 2-iodo-3-nitrobenzoic acid (INBA) and this has been synthesized in two ways in order to incorporate ^{131}I as a tracer.[31,32] In the first method, mercury in anhydro-2-hydroximercuri-3-nitrobenzoic acid was replaced by ^{131}I-labelled iodine; in the second, 3-nitroanthranilic acid was diazotized and the product treated with radioiodine. In preliminary experiments, INBA was applied to a leaf in bean and barley seedlings, and while barley seedlings were practically unaffected, the growth of bean seedlings was impaired in proportion to the dose. As this phenomenon might have been due to uptake in the bean seedling and not in the barley seedling, the point was tested quantitatively by applying INBA to seedlings of bean, oat and maize and measuring the concentrations of activity in various parts of the plants after 8 days. It was found that pure INBA can be recovered from the stem and bud tissues of bean plants treated with INBA, and it is inferred that INBA is absorbed and translocated intact and that it may exert its effect as an intact molecule rather than as a degradation product. It was found that the concentration of INBA in the most rapidly developing parts of both bean and oat seedlings increased with the amount of INBA applied to the plants, but whereas growth was affected in bean seedlings, in oat and maize seedlings it was not. It was concluded that the differences in response could not be explained by differences in the amount of INBA absorbed and translocated but that the mode of action must be quite different in the two types of plant.

The plant growth regulating substance 2,4-dichlorophenoxyacetic acid (2,4-D) has been labelled with ^{131}I; 2,4-dichloro-5-iodophenoxyacetic acid (and also certain derivatives) were synthesized by diazotizing 5-amino-2,4-dichlorophenoxyacetic acid, treating the product with potassium iodide containing 20 millicuries of ^{131}I, and then cooling, filtering and washing with 5% sodium bisulphite and water. After recrystallization from 50% ethanol the yield was 65%.[33]

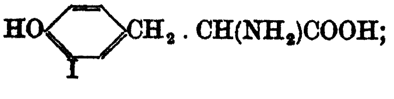
On applying the active iodo-2,4-D to bean seedlings, most was found after three days to be in the more mature parts of the stem. This contrasts with the behaviour of INBA which appeared mostly in the terminal buds of bean plants.[34] These observations are, however, confirmed by the behaviour of 2,4-D labelled with carbon 14.[35] In tests on inhibition of growth in the terminal bud of kidney bean seedlings, it was shown that 2,4-dichloro-5-iodophenoxyacetic acid was only about 60% as efficient as pure 2,4-D. Thus the substitution of iodine modifies the properties of the plant growth regulator quantitatively, but as ^{14}C-labelled 2,4-D behaves similarly in distribution studies it is probable that the mode of action of the ^{131}I-labelled material is the same as that of ordinary 2,4-D.

IODINE AND THE THYROID GLAND

The thyroid gland in mammals secretes a hormone, which has long been known to contain iodine and governs the metabolic rate of the whole body. The development of work on the thyroid gland and its iodine metabolism has been reviewed by Harington.[36] The existence in thyroid tissue of the compound thyroxine was confirmed by its chemical identification and synthesis:[37,38] it is the α-amino acid:-



The thyroxine content of the thyroid gland did not account for all the iodine present and 3,5-di-iodotyrosine was subsequently identified as being the other major organic constituent[39]



for a long time, these were believed to be the only iodine-containing organic compounds in the gland. Using radioiodine ^{131}I as iodide, Morton and Chaikoff[40] demonstrated the synthesis in vitro of di-iodotyrosine and thyroxine by isolated thyroid tissues of sheep, dog and rat. In two or three hours, dog and sheep thyroid slices had converted amounts of the order of 30% of the added iodide into di-iodotyrosine. Rat thyroid was particularly efficient in converting iodide into organic compounds: in 3 hours, about 60% of the activity originally added as iodide appeared as di-iodotyrosine and as much as 12% as thyroxine. To identify thyroxine and di-iodotyrosine after alkaline hydrolysis of the thyroid tissue, unchanged iodide was first eliminated by oxidation in acid solution and extraction with carbon tetrachloride. Then a thyroxine fraction and a di-iodotyrosine fraction were extracted with butanol, the first in strongly alkaline solution and the second at pH 3·5 – 4·0. Pure inactive thyroxine and di-iodotyrosine were added to the respective radioactive fractions and repeatedly recrystallized, the thyroxine as the potassium salt and the di-iodotyrosine from 70% ethanol. The specific activities of successive crops of crystals were found quickly to reach a constant value, and this was taken as evidence for the chemical identity of the radioactive residue and the added pure compound in each case. In fact, although it is evidence of chemical identity, the method of crystallization to constant specific activity is not quite conclusive even when the number of recrystallizations is large, because in any one physical process it is just possible for two different compounds to behave similarly. Later, when Fink and Fink[41] had introduced the method of combined filter paper chromatography and radioactive measurement, with its very high resolution, and had reported the presence of monoiodotyrosine in thyroid hydrolysates, Taurog, Chaikoff and Tong[42] re-examined the matter. They confirmed the presence of a considerable proportion of monoiodotyrosine which must previously have appeared in the di-iodotyrosine fraction. Earlier results of Fink *et al.* showed the presence of other unidentified iodine-containing compounds in rat thyroid hydrolysate, but whether these were present in the original protein or were formed afterwards by reaction of radioiodine with molecules in the solvents employed is not clear.[43]

There is evidence of a sequence of reactions in the biosynthesis of thyroxine in the thyroid. Iodine circulating as iodide is rapidly taken up into the thyroid, as has been often demonstrated by labelling with radioiodine.[44] Iodine administered in the form of iodate and di-iodotyrosine does not enter the thyroid at once, but some does so after an interval.[45] Similarly, if radioactive thyroxine is given, some of the activity does eventually get into the thyroid, but not immediately.[46] In both cases, it is probable that the administered compounds first break down, at least partially, to iodide which is then taken up by the thyroid in the normal way.

In a series of reactions taking place at a steady rate in a tissue, labelling of the initial compound will provide evidence of the order in which compounds are formed one from another.[47] Curves are plotted of specific activity against time for two compounds, and if one is the immediate precursor of the other there will be a definite relationship between their specific activity-time curves. Three criteria may be applied:-

1. When the specific activity of the compound is increasing with time, that of the precursor must be greater.
2. When the specific activity of the compound is maximal, it will be equal to that of the precursor.
3. When the specific activity of the compound is declining, that of the precursor will be still lower.

In this way it has been found that di-iodotyrosine is the biological precursor of thyroxine in the thyroid.[48] Radioiodine was administered as iodide to rats which were divided into groups and killed at intervals, the thyroids of each group being pooled and the di-iodotyrosine and thyroxine extracted. Measurements of specific activities showed that the curve for di-iodotyrosine rose more rapidly than that for thyroxine, passed through a maximum and then cut the curve for thyroxine when that had just about reached its maximum.

Similarly, when confirming the presence of monoiodotyrosine in normal thyroid tissue, it was shown by Taurog, Chaikoff and Tong[49] that the variation with time of the specific activities of the monoiodo- and di-iodotyrosine fractions was consistent with the suggestion that monoiodotyrosine is the precursor of di-iodotyrosine. It appears, therefore, that iodine entering the thyroid as iodide ion is oxidized and forms first monoiodo- and then di-iodotyrosine, two molecules of which undergo an oxidative coupling with the elimination of the side chain of one, so forming thyroxine.

THE CHEMICAL NATURE OF THE CIRCULATING THYROID HORMONE

During the synthesis of thyroxine within the thyroid gland, all the iodinated amino acids remain bound within protein molecules, and for some time it was considered that the circulating thyroid hormone secreted by the gland was this protein itself. However, thyroid tissue given by mouth is capable of relieving the symptoms of lack of thyroid hormone in the blood, and this makes it unlikely that the circulating hormone is thyroglobulin, the protein of the thyroid gland. This protein, when administered orally, would be decomposed in the stomach and could hardly be resynthesized thereafter. A later view that the circulating thyroxine was combined in a polypeptide has also been abandoned in the light of evidence presented by Taurog and Chaikoff[50] that most of the iodine is present in the blood as thyroxine itself. They showed that the circulating iodine could be extracted from plasma into *n*-butyl alcohol directly and was only slightly re-extracted with a 4N-NaOH-5% Na_2CO_3 solution which would take up di-iodotyrosine and any inorganic iodine. When rats received ^{131}I 24 hours before their plasma was extracted with butanol, a radioactive extract was obtained which crystallized to constant specific activity with inactive pure thyroxine. The distribution between two immiscible solvents was also similar to that for pure thyroxine, and very different from that obtained when a peptide obtained from thyroid protein was examined with the same solvent pair. Chromatographic examination of the radioactive butanol extract from the plasma of rats[51,52] has also shown the presence of thyroxine, and it is concluded from all this evidence that thyroxine is the true circulating thyroid hormone. Thyroxine in the blood is associated with particular protein fractions,[53] but there is no evidence of chemical binding, as otherwise the direct extraction from plasma into butanol could hardly occur.

Recently, Gross and Pitt-Rivers[54,55] have demonstrated the presence of 3,5,3′-tri-iodo-L-thyronine in the plasma of human patients who had been undergoing ^{131}I therapy. The material was found to act in the same way as thyroid hormone but was about three times as active biologically as thyroxine itself. The authors suggest that tri-iodothyronine might be the real thyroid hormone, formed by enzymatic de-iodination of thyroxine. It may well be that the similarity of tri-iodothyronine to thyroxine, chemically and in their behaviour in some chromatographic systems, has led to its being so long undetected, just as monoiodotyrosine was long undetected in thyroid tissue.

Active iodine has been used extensively in studies of chemical substances which interfere in various ways with the metabolism of iodine in thyroid glands normal and otherwise. The remarkable advances made over the last decade in this whole field has certainly been largely due to the application of the radioactive tracer method.

CLINICAL USES OF THE RADIOHALOGENS: DIAGNOSIS OF THYROID FUNCTION

By far the greater proportion of the radioiodine, ^{131}I, produced at present is used clinically for the diagnosis and treatment of thyroid disorders. Early experiments[56] by Hertz, Roberts and Evans demonstrated the rapid uptake of iodine-128, administered as iodide, into the thyroids of rabbits and indicated that when the thyroid had been stimulated by injection of anterior pituitary extract the collection of iodine by the thyroid was much more rapid and extensive than was normal. Hamilton and Soley[57] introduced the technique of administering about 50 microcuries of ^{131}I to a patient and following the uptake into the thyroid by means of a Geiger–Müller counter placed in a definite position close to the gland. On normal controls, the activity of the gland rose to a substantially constant value after two days. It was found that the thyroid of a patient with myxoedema took up practically no radioiodine, while patients with various other forms of thyroid abnormality showed marked divergences from normal when the curve of activity in the thyroid was plotted against time. The use of radioiodine as a diagnostic aid has been much developed and is now routine practice for the investigation of thyroid function wherever facilities exist for using it. The use of directional-radiation measurement has been so developed that deposits of radioiodine in thyroid tissue or in metastases from thyroid carcinoma can be located in a patient without operation. In an extension of the use of ^{131}I in thyroid function diagnosis, several authors have given small doses (10 microcuries) of radioiodide solution and measured the excretion in the urine over the subsequent 48 hours.[58,59] Differences in excretion rates are found for different thyroid conditions. This type of diagnostic test may be rather less precise than more elaborate studies but it is simple and suitable for routine application.

RADIOIODINE AS A THERAPEUTIC AGENT

The use of radioiodine isotopes in the treatment of thyroid disease was developed mainly in the United States and the earlier work has been reviewed by Hertz.[60] Both 12·6-hour ^{130}I and 8-day ^{131}I were used at first, but more recently the routine production of the latter from pile irradiated tellurium or from fission products has made it the radioiodine generally used. The order of magnitude of a therapeutic dose is 5 – 50 millicuries.

Radioiodine administered as iodide, with as small an amount of carrier ^{127}I as possible, may be fairly rapidly distributed so that about 50% appears in the thyroid and almost all the remainder is excreted in the urine. That in the thyroid will deliver locally a dose of radiation which may be estimated from the behaviour of a small tracer dose administered during diagnosis. This radiation will destroy thyroid tissue almost exclusively. In the early days of radioiodine therapy, carrier iodine amounting to 2 – 14 mg. ^{127}I was used in the therapeutic dose, but now the amount of carrier is kept as low as possible so that the thyroid gland can take up a larger proportion of the dose.[61]

Even when Hertz reviewed the field, it was concluded that radioiodine therapy was of value in many cases of hyperthyroidism as well as in rare cases of cancer of the thyroid. In most cases of thyroid cancer, the malignant tissue is unable to concentrate iodine sufficiently to permit selective irradiation.

Subsequently, much more experience has been obtained in the therapeutic use of ^{131}I and current practice has recently been described.[62,63] While ^{131}I therapy seems well established in the treatment of thyrotoxicosis, there appear to be some cases of thyroid cancer, particularly when metastases occur, where radioiodine is of value.

BROMINE-82 AS A SOURCE FOR RADIOTHERAPY

In the only other major application of a radiohalogen in therapy, the chemical nature of the material is of no significance. Walton and Sinclair[64] have used high activities, of the order of 500 millicuries, of sodium-24 or bromine-82 in solution for the direct irradiation of malignant tissue in the bladder. The solutions are passed into a rubber balloon which has been inserted into the bladder, and after irradiation the active solution is withdrawn. ^{82}Br is chosen for this purpose because of its short half life and the suitability of the radiations emitted.

LOCALIZATION OF TUMOURS WITH LABELLED COMPOUNDS

If organic compounds labelled with iodine-131 or like radionuclide could be found which would have the property of selective concentration in tumours, for example, in the same way as iodine is concentrated by the thyroid, they would be most useful in facilitating the diagnosis of tumours not otherwise observable from outside the body. Considerable interest was aroused by claims that a high proportion of brain tumours had been localized by using the dye di-iodofluorescein labelled with ^{131}I,[65] though later workers have not had such good results. Other radioactive substances that might be concentrated in tumour tissue have been investigated but so far nothing comparable with the concentration of iodine by thyroid tissue has been found.[66]

INDUSTRIAL USE OF RADIOHALOGENS

The use of radiohalogens in industrial processes has so far been due to their physical rather than to their chemical properties. Usually a radioactive liquid or gas is mixed with another liquid or gas respectively, so that the position of the labelled bulk can be determined by detection equipment such as a portable Geiger counter. The essential point is that radioactive material shall be synthesized having convenient properties of solubility, adsorption and so forth, and the fact that the radioactive nuclide used for labelling happens to be a halogen is incidental. Nevertheless, one or two cases may be mentioned where the transport of radiohalogen-labelled materials has been studied as they illustrate one type of industrial usage. This type of experiment, while rather crude, is important, as it yields the desired information more quickly and cheaply than do more conventional methods.

THE DETECTION OF LEAKS IN TELEPHONE CABLES

In most telephone cables copper wires, insulated by binding with brown paper tape, are twisted together and sheathed with an extruded coating of lead. This assembly may sometimes be further protected with tarred jute and even steel tape. Any hole in the lead sheathing may allow water to enter the cable, destroying the insulation, whether the cable is buried in the ground as is usual in Continental Europe or whether the cable is pulled into ducts as is usual in this country. Even after a cable has been tested in the factory, by pumping up with compressed air while immersed in water, leaks may develop during cable laying, sometimes because particles of foreign matter embedded in the lead sheath work loose when the cable is being bent. A method is therefore required for testing for leaks just after the cable is laid and before it is put into service.

Methyl bromide labelled with ^{82}Br has been used[67,68] successfully for finding leaks in cables laid in both the usual ways, since its properties make it very suitable for the purpose. It is stable chemically, condensible enough to be easily manipulated in cold traps and also to be adsorbed on soil so that it remains for some time just below the surface of the ground above a leak in a buried cable. On the other hand it is not strongly enough adsorbed on the brown paper insulation of the cable to be separated from its carrier gas.

Methyl bromide labelled with ^{82}Br is mixed with nitrogen or air and applied to the cable under a pressure of about 1 kg./cm.^{2} In the case of cables buried at 0·8 metre depth, the activity is detected directly above the leak over an area of about 4 or 5 square decimetres, and the active patch develops in a few hours according to the leak size and the distance from the point of injection. Using 10 mc. of ^{82}Br, leaks of 0·08 to 0·2 lit./min. show up clearly on a portable detecting instrument about 12 hours after injection.

In the case of ducted cables, laid in lengths of about 170 yards, it is only necessary to detect which length is leaking. In this case, after the methyl bromide-air mixture has been injected into the cable and the pressure raised to about 20 pounds per square inch above atmospheric, the air in the cable duct is drawn through charcoal by which methyl bromide is strongly adsorbed at ordinary temperatures. The appearance of activity in the charcoal indicates a leaky length of cable, and the sensitivity of the method in these conditions is much higher than for buried cables: indeed it seems likely that a leak of about 1 c.c. at N.T.P. of gas per hour should be detectable.

WATER TRACING

The problem of tracing water in its passage through soil may be of considerable industrial importance. A tracer substance mixed with water and passed with it underground is likely to be lost in the soil by ion exchange, if the activity is cationic, and by adsorption. As oxygen has no convenient radioactive isotope, the only radioactive label for water which could not be separated from the bulk by either of these two processes is tritium, (radioactive hydrogen of mass 3 and a half life about 12 years). Tritium labelling in water tracing has been proposed but is not yet commonly practised. Water tracing with the dye fluorescein is much used, but here again adsorption may interfere. Greater sensitivity should be achieved using radioactive tracing and for this purpose an aqueous solution of bromoform (solubility 3 g./litre) labelled with ^{82}Br has shown promise. Subterranean streams have also been successfully traced with ^{82}Br and ^{131}I, both as the halide ion.[69]

THE INDICATION OF OIL JUNCTIONS IN PIPELINES

Pipelines used for the transport of oils have frequently to be used successively for different grades of oil product, such as motor fuel, aviation spirit, kerosene etc., and may extend for tens of miles or even one or two hundred miles. When the grade of petroleum product is changed, mixing will occur at the liquid junction so that for an appreciable time oil is delivered which is intermediate between the two standard grades and must be rejected. It is therefore important to determine the arrival of the junction as accurately as possible, so that the minimum quantity of a pure grade of petroleum is discarded with the unusable mixture.

A small amount of an oil-soluble compound labelled with a suitable γ-active radioactive nuclide is injected at the junction of two different grades of oil product, the γ-radiation being energetic enough to allow its detection outside the pipeline. As the junction moves along the pipeline, it spreads out by mixing (not appreciably by diffusion) but at the delivery point detection equipment will show the arrival of the mixture of grades and this mixture can be discarded. When the activity falls, pure petroleum product of the second grade is being delivered and can be directed into the appropriate storage tank.

Among the radioactive materials usable for this purpose, ethylene dibromide labelled with ^{82}Br has been found to be quite suitable. It is chemically stable and in small quantity is unobjectionable in petroleum fuels. The γ-radiation is energetic enough to permit easy detection outside a pipeline. The half life of 35 hours is rather inconveniently short because it necessitates making up a fresh supply of tracer material for each investigation. In a field trial[70] on an 8-inch pipeline pumping kerosene and motor spirit at 2·5 m.p.h. over 39½ miles it was found that the spread of the mixed grades, as indicated by the detection of ^{82}Br activity, occupied 220 yards of piping, this being the distance between the positions where the mixture contained 90% kerosene and where it was 90% motor fuel.

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SECTION XLIV

ASTATINE

By A. G. MADDOCK

The element of atomic number 85, the last halogen, often referred to in the past as eka-iodine, was named Astatine by Corson, McKenzie and Segre, who prepared the first isotope of this element that was identified and studied some of the chemical properties of the element. The name, which was derived from the Greek word αστατοσ meaning 'unstable', emphasizes the instability of all the isotopes of this element towards radioactive decay.[1] The recommended pronunciation of the name is ăś tå tēn and the symbol is At.[2] At the meeting of the Commission on Atomic Weights of the International Union of Chemistry at Amsterdam in September, 1949,[3] it was decided that until such time as a macroscopic quantity of this element is separated the official table should indicate in square brackets the mass number of the most stable known isotope, viz. [210]. Earlier names, based on unsubstantiated claims to the discovery of the element, include Alabamine[4] and Anglohelvetium.[5] As an alternative to the obvious inelegance of the latter name, Leptine, (from λεπτοσ) was suggested.[6]

HISTORY

The history of the discovery of this element shows several similarities to that of francium, element 87. The discovery and interpretation of atomic numbers by Moseley and the establishment of the physical basis of the periodic classification of the elements by Bohr in the early nineteen twenties indicated that a fifth halogen might exist.[7] Consideration of the properties of the neighbouring elements suggested it would probably prove to be radioactive, though no basis for the estimation of its radioactive properties was known at that time. The subsequent search for the element followed two principal lines; one involved chemical studies, usually combined with a sensitive physico-chemical method of detection, especially *X*-ray emission spectroscopy, whilst the other depended on radioactive studies.

It was realized that unless the element possessed a stable or very long-lived isotope it must occur in association with one of the three natural decay series, so that attention was focussed on uranium and thorium minerals. However, some investigators ignored the question of the radioactive character of the element and explored the possibility of its natural occurence in macroscopic quantities. The highly specific character of *X*-ray emission spectra, their sensitivity and the simplicity of the preparation of the samples encouraged the application of *X*-ray emission spectroscopy as a means of detection and analysis.

Early Searches using *X*-ray Emission Spectroscopy.

During 1925 and 1926 Loring and Druce reported an investigation of the minor contaminants of a sample of pyrolusite and two samples of pure manganous sulphate. The chemical treatment employed and the identity of the original materials and of the various fractions examined were rather inadequately described. The primary objective of the investigation was the detection of the then unknown elements of atomic numbers 75 and 93.[8,9] In each case the manganese was removed as the sulphide by passing hydrogen sulphide through a solution of the source material and adjusting the pH to a value high enough to ensure complete precipitation of the manganese. The sulphide precipitate was separated and the supernatant solution evaporated to dryness and ignited. The residue was dissolved in nitric acid and the calcium removed as oxalate. The supernatant solution was again separated, evaporated and ignited. The *X*-ray emission spectra of various samples obtained during these separations were examined by Twyman using an *X*-ray emission spectrograph in the possession of Messrs. Adam Hilger, Ltd. The instrument was not capable of resolving the $L\alpha_1$ and $L\alpha_2$ lines of elements in this region of atomic numbers nor, apparently, could it record the *K* radiation. Various plates were obtained showing lines that were attributed to the *L* radiations of the elements of atomic number 75, 85, 87 and 93, all of which were at that time unknown.[10] Two or three plates gave lines at 1·086 and 0·895 A.;[11] which correspond to the wave-lengths calculated by the authors,[12] and others,[13] for the $L\beta$ and the mean $L\alpha$ radiations from element 85. It was observed that the latter line would also correspond to the $L\beta$ radiation from element 93.[11] The identification of the samples giving these radiations is not made clear in the papers. No attempt was made to follow the movement of the material responsible for the supposed radiations during further chemical separations.

It is now apparent that these results must be attributed to other causes. Indeed the insufficiency of such identification was quickly emphasized by other investigators[14] who noted that, within the resolution of the instrument used, the observed lines could be simulated by the Zn $K\alpha$ and the Hg $L\alpha_1$, $L\beta_1$ and $L\gamma_1$ lines. These lines commonly appear, together with those from silver and other elements, when the usual copper anticathode is used. Another common source of anomalous lines lies in imperfections in the crystal in the spectrograph. It was pointed out[15] that only some seven of a number of unidentified lines on the plates were explained by an hypothesis involving the presence of four previously undiscovered elements in the source material.

In a final review,[16] in which the 1·086 A. line is described as nebulous, Loring withdrew any claim to the discovery of element 85.

About the same time the dissolved salts of the Dead Sea were examined for their content of elements 85 and 87.[17] A sample of water from the northern end of the sea was taken during the period of maximum density, when its density was 1·2089. All metals, except the alkali metals, were removed and the chloride in the residual liquor fractionally precipitated as silver chloride. The first fractions were examined by *X*-ray emission spectroscopy but no trace of lines due to element 85 could be found. In 1927 Herzfinkiel reviewed the evidence and concluded that the existence of element 85 was unproved. He described an unsuccessful search conducted in collaboration with Lobanow. Several iron and platinum minerals were examined. The *X*-ray spectroscopy was carried out by Dauvillier.[18]

Unsuccessful Radiochemical Searches

On investigating the possible radiochemical derivation of astatine, Hahn observed that the currently recognized radioactive decay process could only produce isotopes of element 85 either by α-decay of an isotope of the unknown element 87, or by β-decay of an isotope of polonium.[19] Speculation on the origin of the nitrogen generally associated with uranium minerals led to the suggestion of a disintegration process involving the emission of nitrogen nuclei.[20] Such a process occurring in uranium I would produce an isotope of element 85. No evidence supporting such an hypothesis has ever been obtained. The existence of a stable or very long-lived polonium isotope could not be excluded. Hevesy discussed the α and β stability of the isotopes of elements in this region of atomic numbers,[21] and emphasized that no decision could be taken regarding the existence of stable isotopes of either polonium or element 85. The possible genesis of element 85 by α-decay of element 87 linked the searches for these two elements.

No evidence for a long-lived isotope of the element in either of the uranium decay series could be obtained.[22] Iodine was used as carrier; it was incorporated in a sample of Katanga pitchblende by evaporation from a solution of potassium iodide, 2 mg. of iodine carrier being used for 10 g. of mineral. The iodine was separated by volatilization in a stream of chlorine, followed by precipitation as silver iodide. A recovery of about 80% was obtained. The *X*-ray emission spectrogram of the product showed no sign of lines due to element 85, although the $L\alpha$ line should have been noticeable if the ore contained 1 part of the element in 10^9 parts of ore.

A posthumous publication of Anderson,[23] edited by his collaborator Keel, described a similar investigation of a number of minerals in which, however, the products were examined for radioactivity and not by *X*-ray emission spectroscopy. The substances investigated were pitchblende, thorite, a source of Ra-*D* prepared from old radon tubes, and a variety of sulphidic minerals including stibnite and antimonite. The pitchblende and thorite samples were fused with alkali and the melt leached with a very dilute solution of potassium iodate, to provide the carrier iodine. The extract was reduced and the iodine separated either by precipitation as silver iodide or, after re-oxidation to the elemental state, by solvent extraction or sublimation. The sulphidic minerals were dissolved in nitric acid and the carrier again added as iodate. After reduction with hydrazine sulphate the iodine was separated as before. Similar procedures were adopted for the Ra-*D*. The recovery of the carrier was good. All the products were examined for radioactivity by means of a demountable Geiger counter, so that even the least penetrating radiation should have been recorded. No activity that could be attributed to element 85 was detected. The Ra-*D* separations were complete in about 1½ hours; the time taken for the other separations is not given.

A claim to the separation of a macroscopic amount of element 85 from Travancore monazite has been made.[24] The substance was separated during a supposedly successful search for the thorium series analogue of Ra-*F*. The author suggested the name 'Dakin' for the element. From the account[25] of the properties given it is not possible to deduce the nature of the substance that was obtained.

Other Attempts at Physical Detection.

In common with that of the rest of the then missing elements, the discovery of element 85 was claimed by investigators using the discredited magneto-optic method of analysis.[26] The supposedly responsible isotopes of the element were enumerated and an attempt was made to fit them into the radioactive decay series.[27]

Toshniwal[28] suggested that two inexplicable lines, at 2012 and 1969 A., observed during the photo-dissociation of iodine vapour, should be attributed to element 85. The lines were probably due to impurities.

In 1934 Hulubei and Cauchois[29] examined the direct quantum emission from radon and its decay products in the wave-length region from 15 to 1300 *X*., using a curved crystal focussing spectrograph with photographic recording. If the plates are suitably screened from the direct radiation from the source, such a spectrograph will detect even very infrequently excited radiations. Control experiments with an X-ray tube having a molybdenum anticathode showed that all the forbidden $K\beta$ lines, including the $K\beta_8$ and $K\beta_9$ lines, could be found by an exposure of a few hours. The dispersion of the instrument was about 1 X./mm. in the third order and the molybdenum $K\beta_5$ doublet was resolved in the first order. A two hour exposure with a 250 m.c. radon seed revealed several lines within the above wave-length range. Five years later, after the exposure of many more plates both on the original and on other spectrographs, several of the lines were identified with those to be found in the X-ray emission spectra of lead, bismuth or polonium, all of which elements appear amongst the radon decay products.[30] However, three lines, at 1082·6, 892 and 151 X., could not be attributed to any known element. It was suggested that these were the $L\alpha_1$, $L\beta_1$ and $K\alpha_1$ lines of element 85. The observed wave-lengths were in good agreement with those calculated for element 85 by extrapolation from the data obtained in the same experiments for the radiations from elements 82, 83 and 84, or by interpolation from existing data for bismuth and radium. It was suggested that element 85 must be present in the radon decay products. In the following year[31] these authors claimed priority for their discovery, in view of Minder's observations on the β decay of radium-A (see below). Valadares[32] confirmed these observations and reported additional lines at 875, 880 and 917 X. which he attributed to the $L\beta_5$, $L\beta_3$ and $L\beta_4$ lines of element 85. It was impossible to look for the $L\gamma_1$ line because it coincides with the $L\gamma_4$ line of bismuth. A much more detailed account of the earlier experiments was published by Hulubei.[33,34] She observed that 10^{-10}g. of polonium could be detected by excitation at an anticathode and that nuclear excitation of the X-radiation of element 85 might be much more efficient, so that very minute amounts could be detected. The best results were obtained with a spectrograph of radius 75 or 150 cm., with heavy protection to avoid parasitic blackening of the plates. Twenty-four hour exposures with a 200 m.c. source of radon were used for the measurements on the radiations. The name 'Dor' was proposed for the element.

Since it is now known that an isotope of element 85 is found as an occasional branch product amongst the radon decay products, it is quite possible that some lines of its X-ray emission spectrum may be found in the radiations from radon seeds. Although the branching ratio for the production of element 85 is very small, it is indeed quite possible (if, for example, the β-decay of radium-A is associated with a heavily internally converted γ radiation) that every atom of element produced emits a quantum of X-radiation. Nevertheless, it is very doubtful if such weak radiation could be detected, even with the focussing spectrographs described. Great care must be taken in the interpretation of X-ray emission spectra. For instance, several inexplicable satellite lines were observed to accompany the bismuth lines.[29] These were attributed to the effects of orbital rearrangement in the nascent atoms. It is even possible that some of the observed radiations were of nuclear origin. These and other possibilities have been discussed by Hulubei.[35]

Element 85 as a Branch Product in the Natural Decay Series.

The discoveries of artificial radioactivity and of the neutron were a powerful stimulus to radiochemical research, including the study of the naturally radioactive elements. Although nuclear theory did not develop sufficiently to predict the radioactive characteristics of isotopes of the heavy elements, empirical studies of the systematics of α- and β-decay revealed regularities sufficiently marked to permit confident interpolation of the radioactive constants of the isotopes of both the known and unknown elements.

It thus became recognized that all the isotopes of element 85 would be radioactive.

The conditions for β-activity were found to be much the same for all nuclei. The regularities in the distribution of stable nuclei, especially those of odd atomic number, were discovered. The application of these rules to element 85 suggested that the isotopes of mass number 213, 215 and 217 would be stable to either kind of β-decay. Two of these nuclei might occur as decay products in the missing $4n + 1$ decay series, one member of which, ^{233}Pa, had by this time been discovered.[36]

Another empirical rule advanced by Turner[40] stated that the β^--stable isotopes of an odd element are given by one or two of the three mass numbers $A + 1$, $A - 1$, $A - 3$, where A is the heaviest β^--stable isotope of the preceding element. This rule indicates that the lighter isotopes of element 85, 211, 213 and 215 should prove β^--stable. Schintlmeister explored the relation between the β^--decay energy and the isotope number ($I = A - 2Z$) and erroneously concluded that Ra-*A* and Th-*A* should be stable to β^--decay.[37] On the other hand Minder showed that isotopes for which $(A - Z)/Z > 1{\cdot}56$ are β^--active and concluded that Ra-*A* and Th-*A* should exhibit β^--activity.[39]

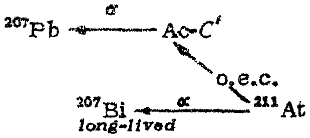
Because of the complex relation between the β^--decay energy and the half-life, no reliable prediction could be made of the β^--decay half-lives of the above two isotopes: nevertheless, Turner estimated their β^--decay half-lives and hence the β^-/α branching ratios. For the former isotope he anticipated a half-life for β^--decay of $\sim 0{\cdot}1$ sec. so that the β^-/α branching ratio should be $\sim 5 \times 10^{-3}$. Th-*A*, and probably Ac-*A*, should show extremely small β^-/α branching ratios. The production of an isotope of element 85 by decay of the product of radiative thermal neutron capture in radium was considered.[38]

When the α-decay energy is plotted against the atomic and mass numbers in a three dimensional graph, the points lie on a smooth concave surface from which the α-decay energies of unknown isotopes can be estimated. The relatively simple relation between the α-decay energy and the half-life permitted more accurate prediction of the radioactive characteristics of these nuclei. In this way it was found that the 30 year natural actinum, ^{227}Ac, should show measurable α-activity and that the decay product, an isotope of the then unknown element 87, should in turn show some α-activity, as well as β^--activity, producing thereby an isotope of element 85.[37,39,40]

In 1940 Minder claimed to have detected an increase in the β^--activity of radon with time, during the first 13 minutes after purification of the radon, greater than could be ascribed to the growth of Ra-*B* and Ra-*C*. This additional activity appeared to be due to a radiation that was absorbed by only 1 mm. air equivalent. He suggested that the activity was due to Ra-*A*. Except for the doubtful suggestion that the coagulation of a starch solution by radon might be due to the element 85 so formed, he could not find any chemical evidence for the formation of element 85. However, he proposed that the element be called Helvetium.[41] Turner[40] doubted the validity of this claim because the small range of the radiation was incompatible with his expected β^--decay energy of Ra-*A*. Repetition of Minder's experiments by Karlik and Bernert failed to confirm his results.[42,43]

THE DISCOVERY OF ASTATINE

Until the second and larger cyclotron began working at the University of California at Berkeley, no accelerator was capable of accelerating helium ions to a sufficiently high energy to surmount the coulomb barrier of the heavy elements and so reach an energy region where the cross-section for α-induced nuclear reactions became appreciable. Upon completion of the 60 in. cyclotron one of the first nuclear reactions of the heavy elements to be studied was the α-bombardment of a bismuth target. The bombardment produced two new α-active species of range 6·5 and 4·5 cm. in air at N.T.P., 60% of the α-activity belonging to the long range group and 40% to the short range group of α-particles. Both activities decayed with a half-life of 7·5 hr.[44] The activity could be separated from the target by distillation and was also shown to be separable from mercury, lead, thallium, bismuth and polonium. The possibility of fission was excluded by both chemical and physical considerations. The chemical properties described in this first publication[45] subsequently proved rather inaccurate but the α-activities were correctly ascribed to a 7·5 hr. isotope of element 85, subsequently called astatine (see page 1064), ^{211}At. The 4·5 cm. particle is emitted by the direct α-decay of the isotope. An alternative mode of decay, by orbital electron capture, produces a polonium isotope, actinum-*C′*, which has a very short half-life and emits the penetrating 6·5 cm. α-particles.



THE NATURAL OCCURRENCE OF ASTATINE

The literature of the study of the β^--activity of the *A* products in the natural decay series is now quite extensive, but only one of the three cases seems adequately established. Minder and Turner pointed out that the proton–neutron ratios in Ra-*A*, Th-*A* and Ac-*A* were large enough to make β^--activity very likely (see page 1068). The earliest claim to the discovery of the β^--activity of Ra-*A* was not confirmed.[41–43] Subsequently evidence of the β^--activity of Th-*A* was reported by Leigh-Smith and Minder.[5] The thoron from a 40 m.c. source of radio-thorium was blown between oppositely charged copper sheets for 20 minutes; the supposed astatine was sublimed from the negative electrode at 180°C. and condensed on a cooled silver wire. The wire was then examined in a Wilson cloud chamber. After 10 – 20 minutes α- and β^+-tracks were abserved whose origin lay in the gas or on the walls of the chamber. The α-tracks appeared in pairs, sometimes accompanied by a β^--track. Karlik and Bernert were unable to repeat this experiment, although Leigh-Smith and D'Agostino reaffirmed their claim five years later.[46] It is now known that the half-life of the astatine isotope ^{216}At is too short for detection to be possible by means of such an experiment.

The following year a study of the energy of the α-particles emitted by Ra-*A* produced evidence of a very short-lived daughter product emitting energetic α-particles.[47] The Ra-*A* sources were prepared by 10 – 15 second exposures of a charged foil in 100 m.c. of radon. The α-particles were observed by means of an ionization chamber with a four stage electrometer amplifier and the output was displayed on a cathode ray oscilloscope. A new group of α-particles, easily distinguished from those of Ra-*C′*, of energy 6·63 M.e.V. was detected. The decay of this activity followed that of the Ra-*A*, indicating that the emission arose from a β^--decay product of Ra-*A* whose half-life could not exceed a few seconds. The proportion of these α-particles determined[48] the β^-/α ratio for Ra-*A* as $3{\cdot}3 \times 10^{-4}$, in reasonable agreement with Turner's estimate of 5×10^{-3}.[40]

Attempts at the direct detection of the β^--radiation have been unsucessful.[49,50]

Two alternative interpretations of the above observations are possible

Radon itself might be β^--active and the energetic α-particles could be emitted by either the francium daughter of the radon or by the astatine isotope formed by α-decay. Alternatively it is conceivable that the energetic particles are emitted by a nuclear isomer of Ra-*A*. The first of these alternatives has been disposed of, at least in so far as a francium isotope of half-life more than a few minutes might be involved: separation of an alkali metal fraction from the radon decay products failed to separate the new active species.[51]

Soon after the discovery of β^--branching of Ra-*A*, Karlik and Bernert reported the β^--branching of Th-*A* and later of Ac-*A*. The β^-/α ratio for Th-*A* was reported as $1{\cdot}35 \times 10^{-4}$ and the short-lived ^{216}At produced was found to emit α-particles of 7·63 M.e.V.[52] The β^-/α ratio for Ac-*A* was given as $\sim 5 \times 10^{-6}$ and the particles emitted by the short-lived ^{215}At had energy 8·4 M.e.V.[53,54] The improbability of this interpretation of the former investigation was pointed out by Flügge and Krebs.[55] Each β^--branch rejoins the main decay chain at the *C* product, so that if each leads to the ground state of the *C* product the energy released should be the same by either route, since each involves the emission of one α- and one β^--particle. For Ra-*A* the total disintegration energy (the sum of the kinetic energies of the α-particle and the recoiling nucleus) is 6·09 M.e.V., and the total disintegration energy of Ra-*B* is 0·96 M.e.V. The total α disintegration energy for the ^{218}At is 6·75 M.e.V. Thus the β^--disintegration energy of Ra-*A* must be 0·3 M.e.V. This value is compatible with the observed branching ratio for a simple allowed β^--emission. A similar calculation for Th-*A* shows that the observed α-disintegration energy of the ^{216}At exceeds the combined disintegration energies of the *A* and *B* products. In the case of Ac-*A* about 0·75 M.e.V. is available for β^--decay.

Karlik and Bernert acknowledged these anomalies but suggested that nuclear isomerism of Th-*C*, and possibly Ac-*C*, might account for them.[56] However, it has been observed that if nuclear isomerism be invoked the β^--activity hypothesis is superfluous. One may postulate that the decay of thoron or actinon produces a small proportion of a nuclear isomer of the *A* products. The decay of these isomers leads to the energetic α-particles.[57,58] This latter hypothesis now seems the most plausible explanation of Karlik and Bernert's results. Both ^{216}At and ^{215}At have been detected as short-lived decay products in the collateral decay chains derived from ^{228}Pa and ^{227}Pa respectively. The α-particle energies from ^{216}At and ^{215}At have been determined as 7·79 M.e.V.[59] and 8·00 M.e.V.[60] respectively. Both these values are different from Karlik and Bernert's values by several times their probable error. Karlik has re-examined her evidence in a review of astatine.[61] Avignon confirms the branching Ac-*A*, giving $\beta^-/\alpha = 0{\cdot}9 \times 10^{-7}$, and reports that the characteristics of the resultant ^{215}At are in agreement with those of the isotope obtained by ^{227}Pa decay.[62] Feather has estimated the β^-/α ratio as $\sim 6 \times 10^{-7}$ on theoretical grounds.[58] Such a branching ratio would be consistent with an allowed β^--emission of 0·75 M.e.V. energy.[58]

It is possible that the β^--decay of Ra-*A* is more complex than has been described. The discoverers remarked on the probable complexity of the α-particle spectrum of the ^{218}At decay. Walen has re-examined the α-spectrum of the active deposit from radon using a proportional counter and oscilloscope.[63] He concludes that the β^-/α ratio for Ra-*A* is 2×10^{-4} but that the ^{218}At also exhibits β^--activity with $\beta^-/\alpha \sim 10^{-3}$. The product of this mode of decay, ^{218}Rn, is described as an α-emitter of half-life 1·3 seconds.[64] However, ^{218}Rn formed as a decay product in the collateral series derived from ^{230}U has been found to have a half-life of 0·02 seconds.[65]

To summarize the present position: Ra-*A* is β^--active with β^-/α ratio $3{\cdot}3 \times 10^{-4}$; the product of the β^--branch is ^{218}At, an isotope of half-life 0·02 seconds emitting α-particles of 6·63 M.e.V. It is possible that this isotope also exhibits β^-/α branching. It is unlikely that Th-*A* shows similar behaviour. The case of Ac-*A* awaits further experimental evidence.

Studies of the systematics of α- and β-decay have led to the conclusion that the natural francium isotope, ^{223}Fr or Ac-*K*, formed by α-decay of actinium, should also be active.[37,57,64] Recently Hyde and Ghiorso have detected this activity.[66] They have determined the α/β^- ratio for ^{223}Fr as $\sim 4 \times 10^{-5}$. The half-life of the daughter ^{219}At is given as 0·9 min.: it is sufficiently long for the separation and chemical identification of the activity. The experiments were conducted with a 20 m.c. actinium source. The ^{219}At emits α-particles of 6·27 M.e.V., decaying to give ^{215}Bi, a β^--active body of half-life 8 minutes. ^{219}At also undergoes β^--decay to produce ^{219}Rn, $\beta^-/\alpha = 0{\cdot}03$. There is no spectroscopic evidence for stellar astatine.

NUCLEOGENESIS OF ASTATINE ISOTOPES

Although not quite the longest-lived, ^{211}At is, from the point of view of the chemist, the most important isotope of astatine. It is prepared by the bombardment of bismuth with helium ions; ^{209}Bi (α, 2*n*) ^{211}At. The threshold for the reaction is about 21 M.e.V.,[67] and the cross-section for the reaction rises to about 0·9 barns (see page 1002) at 26 M.e.V. If the helium ions are accelerated to more than 28 M.e.V. the threshold of the (α, 3*n*) reaction is passed and ^{210}At is produced. This isotope decays by orbital electron capture, producing polonium, and emits a 1 M.e.V. γ-ray. Its half-life is 8·3 hours. Therefore the product has greater radiochemical purity if the bombarding helium ions do not exceed 28 M.e.V. The product of the (α, *n*) reaction, ^{212}At, is too short-lived to contaminate the products after separation from the bismuth. The helium ion beam in the accelerator is usually contaminated with deuterons so that the target usually contains ordinary polonium formed by the reaction ^{209}Bi (*d*, *n*) ^{210}Po. Some polonium may also be formed by the reaction ^{209}Bi (α, *p*2*n*) ^{210}Po.

Astatine, ^{211}At, decays on the one hand by *K*-capture to give Ac-*C*′ and on the other by α-decay to give a long-lived bismuth isotope ^{207}Bi decaying by orbital electron capture. The decay process has been observed.[68]

The formation of ^{219}At and ^{218}At has already been discussed in connexion with the natural occurrence of astatine (see page 1068 and above). The isotopes of mass numbers 214, 215 and 216 have been identified as short-lived α-active products in the collateral decay chains derived from ^{116}Pa, ^{117}Pa and ^{228}Pa respectively.[59,60]

The isotope ^{217}At is also a short-lived α-active body, but it is noteworthy as being the only astatine isotope formed in the main branch of a principal chain in the radioactive decay series. It is found in the products of the $4n + 1$ decay series and is therefore formed by the decay of ^{237}U or ^{233}U.[69–71] It has a short half-life, 0·018 sec., and emits α-particles of 7·023 M.e.V.

The isotope of mass number 213 has not yet been described. All the remaining known isotopes from mass number 200 – 212 have been prepared by the bombardment of bismuth with helium ions of appropriate energy.[73] They are generally so short-lived as to be of little chemical interest. The isotope ^{209}At has a half-life of 5·7 hours and the decay products, ^{205}Bi and ^{205}Pb, have been investigated:[74] ^{208}At exists as two nuclear isomers of half-lives 1·7 and 7·0 hours and is interesting as a daughter product of the relatively stable low-mass isotope of francium, ^{212}Fr, half-life 19·2 minutes, formed by bombardment of thorium with 250 M.e.V. protons.[75] Two lighter isotopes of astatine, ^{203}At and ^{205}At, have been prepared by the bombardment of gold with accelerated stripped carbon nuclei; ^{197}Au (C^{6+}, 4*n*) ^{205}At and ^{197}Au (C^{6+}, 6*n*) ^{203}At.[76,77] The radioactivity of astatine has been discussed by Maddock.[78]

THE CHEMICAL PROPERTIES OF ASTATINE

Isolation of Astatine

The bismuth target must be cooled efficiently so that the hean generated by the ionic bombardment does not volatilize the product. Two kinds of target have been used; one is an aluminium disc coated by evaporation with a thin layer of bismuth, the other is made by pressing bismuth oxide into a number of holes in a copper plate. The astatine is separated from the bismuth by evaporation in vacuo at the melting point and is condensed in a glass trap at the temperature of liquid nitrogen. A second distillation is carried out at room temperature. The double distillation reduces the polonium to 10^{-6} of its initial value. The thick target yield (40 mg./cm.^{2} bismuth) at 28 M.e.V. is $1{\cdot}2 \times 10^9$ disintegration/minute/μamp.-hour.[79]

Alternatively the bismuth oxide may be dissolved in perchloric acid and the bismuth and some of the polonium precipitated by the addition of phosphoric acid, but this method of separation does not remove the polonium so efficiently.[80]

The Estimation of Astatine

Astatine is most conveniently estimated by means of its α-activity. Material of high specific activity is best measured on thin samples, not more than 1 mg./cm.^{2} thick, mounted on a metal disc. Care must be taken to avoid loss of astatine by evaporation.[79] Materials of lower specific activity are better measured with samples thicker than the range of the α-particles.[80] The photographic plate method should also be suitable for the estimation of astatine.[81]

Very low specific activities may be measured, if large quantities of the material are available, by means of the K X radiation of the Ac-C', using an ionization chamber or scintillation counter.[79] Biological materials can be estimated, after destruction of the tissue by perchloric acid, by co-deposition on a tellurium precipitate or by separation on a silver foil. No loss by volatilization has been experienced during destruction of the tissue[82] and recoveries of 98% are reported.

The Properties of Astatine

Since the half-life of ^{211}At is so short, macroscopic quantities of the element have not been separated and information is available only from tracer experiments. Since such experiments are notoriously liable to misinterpretation, emphasis will be placed on the experimental results. As 650 atoms of astatine give 1 α-disintegration/min., very large activities would be required to prepare solutions of normal strength. Thus a 1 M-astatine solution would give $1{\cdot}54 \times 10^{16}$ α-particles/min./c.c. Such an activity would lead to considerable radiation effects including continuous production of hydrogen peroxide. In fact, the strongest solution so far employed has been but 10^{-8} M. and most investigations have been confined to solutions between 10^{-11} and 10^{-15} M. At such dilutions the effect of concentration on the thermodynamic properties is very large and the extrapolation of the results to macroscopic behaviour is correspondingly uncertain. These uncertainties will arise if dissociation or ionization effects occur or if the reaction involves a change in the number of molecules of the astatine compounds. Some of the conclusions drawn from the present experimental data will no doubt later be proved erroneous.[79,80,83,84]

Volatility

The volatility of astatine from dry solid surfaces depends on the nature of the surface. The true volatility of astatine is most nearly displayed on clean glass or similar substrates. The evaporation from these surfaces is roughly exponential with a half-life of about 1 hour at room temperature. From gold or platinum the half-life is about 16 hours. After solution in nitric acid there is still a considerable loss on evaporation, because most of the astatine remains in the elemental state. The half-life for evaporation of the astatine from glass rises to 4 hours at 80°C. A nearly constant loss of 26% is experienced on drying such solutions on a platinum tray.[79]

The difference in the behaviour of astatine and iodine is very noticeable upon distilling aqueous solutions. Distillation of 90% of the aqueous phase volatilized the following fractions of the astatine present:-

14% from 16 M-nitric acid,
2% from 5 M-nitric acid containing 3 mg. I,
30% from 12 M-hydrochloric acid,
9% from 18 N-sulphuric acid,
0% from 60% perchloric acid,
93% from 0·5 M-sulphuric acid + 0·05 M-Fe^{2+} aq.

The whole of the iodine was volatilized from the 5 M-nitric acid solution in less than 10% of the solution.

From carbon tetrachloride and benzene solutions 36 and 38% of the astatine, respectively, accompanied the first 90% of the distillate.[79,80,83]

Adsorption on Metals

Astatine vapour is also adsorbed strongly at room temperature, possibly with chemical reaction, on silver, gold and platinum surfaces. At 325°C. the adsorption on silver is much stronger and on gold relatively weaker. It seems probable that the astatine reacts with a clean silver surface.[79,83]

Valence States in Aqueous Solutions

In addition to solutions of elemental astatine there is evidence of three valence states, the astatide ion, At^-, and two anions derived from positive oxidation states, probably AtO^- and AtO_3^-.

The sign of the ions containing astatine has been shown to be negative in the following solutions; 1 M- and 0·1M-nitric acid, phosphate buffers at pH 3,5, 7,9,11 and 13, 0·1 M-nitric acid saturated with sulphur dioxide, 0·1 M-caustic soda treated with sodium sulphite, 0·1 M-nitric acid after oxidation with hot potassium persulphate, 0·1 M-caustic soda oxidized by sodium hypochlorite and 0·5 M-nitric acid oxidized by bromine. In each case the sign was determined by means of a three compartment migration cell in the form of a U tube and fitted with platinum electrodes.[79]

Astatine solutions show critical deposition potentials of −1·22 volts at the cathode and −1·45 volts at the anode.[79] These deposition potentials were measured by the method of Joliot.[85] The nature of the electrode reactions is unknown. The cathodic deposition is reversible and is observed only in solutions that have been oxidized by dichromate. Elemental solutions or those that have been more vigorously oxidized by persulphate do not show the cathodic deposition. The anodic reaction takes place in all solutions of astatine. The electrodes used in these experiments were of thin gold foil.[79]

Co-deposition and Oxidation-Reduction Reactions

Astatine is adsorbed strongly on dust and many kinds of precipitates. Such effects are reduced by the presence of iodine as carrier. However, in clean vessels solutions of astatine in 10 M-nitric acid, 0·5 M-nitric acid and

0·1 M-caustic soda show no losses on centrifuging at 2000 *g*. Elemental astatine is removed from solution by precipitation of elementary tellurium, metallic silver and various heavy metal sulphides, but the efficiency of removal is greatly reduced by the presence of iodine as carrier, indicating that adsorption is responsible.[80,82–84]

The astatide state is obtained on reduction by sulphurous acid, nascent hydrogen or, less efficiently, arsenious acid. A 0·25 M. solution of ferrous sulphate will not reduce astatine to the astatide state. The astatide ion is completely removed from solution by precipitation of silver iodide at all pH values. Thallous or palladous iodide precipitates are equally effective. If, however, the conditions of reduction and precipitation are such that some elemental silver is precipitated the whole of the astatine will be found on the free silver.[79,80] Precipitation of silver iodide does not remove elemental astatine from solution. Re-oxidation of the astatide ions to astatine can be effected by ferric ions.

A positive oxidation state, an oxy-anion, is obtained by oxidation with bromine or dichromate or, much more slowly, with cold nitric acid or ferric ions. At $\text{pH} > 13$ astatine solutions disproportionate to give astatide ions and the same oxidation state. No characteristic co-deposition reactions have been discovered, although this oxy-anion is carried down on a silver iodide precipitate. By analogy with the other halogens this state may be the AtO^- ion. Stronger oxidizing agents such as persulphate or hypochlorous acid give a second oxy-anion which, unlike the first, is efficiently co-deposited on a silver iodate precipitate. This higher valence state is supposed to be the AtO_3^- ion.

A number of miscellaneous co-deposition reactions have been described.[83,84] Lead and thallium can be separated from solutions of the element by precipitation as the chlorides without loss of the astatine. Tellurium precipitated by sulphur dioxide in 3N-hydrochloric acid carries down the astatine but effects separation from polonium. The tellurium can be separated subsequently by precipitation with sodium stannite solution, when the astatine remains in solution. Astatine co-deposits on bismuth, mercury, silver and antimony sulphides in 6N-hydrochloric acid. In alkaline solution the deposition is incomplete. It is also carried down with a number of hydroxides from both the elemental and oxidized solutions. Lanthanum hydroxide carries down very little elemental astatine but removes a large part of the activity from an oxidized solution of the element. It is suggested that $La(AtO_3)_3$ is rather insoluble. Fractional hydrolysis of bismuth nitrate in solutions of elemental astatine gives first fractions enriched in astatine. Copper or bismuth foils remove some astatine from 0·25 N-nitric acid solution. All these results were obtained in the absence of iodine as a carrier.[79,83]

The Solvent Extraction of Astatine

Partition studies with astatine have proved one of the most powerful and reliable techniques of investigation. The partition coefficient of elemental astatine between carbon tetrachloride and 0·01 M-nitric acid is about 90 and between benzene and the same aqueous phase about 200. In making measurements the astatine, purified by volatilization at room temperature, was dissolved in the organic solvent and repeatedly extracted with the aqueous phase. The first few partitions give lower values but the partition coefficient soon reaches a nearly constant value. The reproducibility of the experiments is poor, probably because of the effect of minute fortuitous amounts of oxidizing or reducing agents in the system.

Extraction with a 0·1 M-caustic soda solution reduces the partition coefficient to about 1·0, presumably because of the disproportionation reaction to give At^- and AtO^-. Reacidification to 0·1 M. in nitric acid raised the coefficient to 25 for carbon tetrachloride, indicating a reversible equilibrium.

The effects of various oxidizing and reducing agents on the solvent extraction of astatine have been studied. Astatine dissolved in an organic solvent was extracted first with 0·01 M-nitric acid and then with the aqueous phases indicated in Table I, which shows the values of the respective partition coefficients.[79]

TABLE I.- EFFECT OF OXIDATION OR REDUCTION OF ASTATINE ON PARTITION COEFFICIENTS

Solvent	Partition coefficient with 0·01 M-nitric acid	Aqueous layer	Partition coefficient with aqueous layer
1. Benzene	91	0·25 M-ferrous sulphate in 0·01 M-nitric acid.	89
2. Benzene	200	Saturated sulphur dioxide in 0·01 M-nitric acid.	3
3. Benzene	200	Cold 0·01 M-potassium persulphate.	5
4. Benzene	200	0·1 M-potassium persulphate at 50°C.	0·1
5. Benzene	50	3 M-hydrochloric acid.	0·66
6. Benzene	200	0·1 M-potassium iodate in 0·01 M-nitric acid.	16
7. Carbon tetrachloride	90	Saturated arsenious acid; 20 mins.	31
8. Carbon tetrachloride	50	1·1 M-potassium iodide in 0·01 M-nitric acid.	0·4
9. Carbon tetrachloride	85	0·25 M-ferric nitrate in 0·01 M-nitric acid.	2
10. Carbon tetrachloride	85	0·1 M-bromine in 0·01 M-nitric acid.	0·05

THE PHYSICAL PROPERTIES OF ASTATINE

Until macroscopic quantities of astatine become available, few of the physical properties of the element or its compounds can be measured. Such properties as have been described have been interpolated or extrapolated, by various theoretical or empirical treatments, from the data available for nearby or homologous elements.

Early calculations concern the possible atomic weight of the element.[86-88] The first and second ionization potentials of the element are calculated[89] to be 9·5 and 18·2 volts respectively.[90,91]

The melting point and boiling point of the element are predicted to be: m.p. 411°C., b.p. 299°C.[92] The fundamental frequency of the diatomic astatine molecule is estimated to be 138·4 cm^{-1}.[93] The polarization of the astatine hydride molecule has been discussed.[94]

NUCLEAR PROPERTIES OF ASTATINE

The principal radioactive characteristics of the astatine isotopes are included in the table of isotopes of the halogens (see page 962). Certain other nuclear properties and their relation to the radioactive properties of the other heavy elements will be briefly considered in this section. Shchukarev discusses the analogy between the absence of stable isotopes of the odd elements Tc, Pm, At and Fr and the absence of stable odd isotopes of the even elements A and Ce.[95] However, this analogy may be illusory, since apart from the α-instability common to the heavy elements, the isotopes ^{215}At and ^{219}Fr are very probably stable both to β-decay and orbital electron capture.[58,96] Spitzyn concludes that ^{211}At should be the most stable isotope of astatine on the basis of the trend of the n/p ratios in the predominant stable isotopes.[97,98] It will be observed that contrary to this prediction and others, ^{210}At is the most stable isotope. Way tabulates the binding energy of the proton and neutron in the astatine isotopes.[99]

The variation of the disintegration energy of the active astatine isotopes with the mass number is in excellent agreement with what is known of the other heavy elements. Thus the curve shows the usual sudden change at a neutron number $(A-Z)$ of 126, arising from the abrupt change in nuclear radius corresponding with the completion of a nuclear shell.[100,101]

The disintegration energy falls from ^{200}At to a minimum value at ^{210}At, whence it rises abruptly after ^{211}At, reaching a maximum value at the unknown, but very probably short-lived, ^{213}At. Thereafter it falls steadily until β^--instability dominates the decay process beyond ^{219}At.[102,103] A plot of the α-disintegration energy versus the half-life for the astatine isotopes yields the usual smooth curve.[96,104]

BIOLOGICAL BEHAVIOUR OF ASTATINE

Very shortly after the discovery of astatine Hamilton began to study its biological behaviour. It is, perhaps, surprising, in view of the appreciable differences in chemical properties between iodine and astatine, that astatine concentrates in the thyroid gland,[44,105] though it is not concentrated quite as efficiently as iodine by the thyroid gland of the rat or guinea pig.[105,106] All the halogens, except fluorine and the pseudo-halogen, thiocyanate, show this property and each can replace the other by a kind of mass action effect.[107] If the iodine is replaced in this way thyroid hyperplasia will result. Hamilton and his collaborators have made an extensive study of the effects of ^{211}At injection into various animals, including human beings, with a view to its possible application in clinical treatment.[108-116] The haematological effect of astatine, ^{211}At, has been described by Kramer.[117,118]

REVIEWS

Numerous reviews of different aspects of astatine have appeared.[119-137] Many of these have only ephemeral interest, but two that are especially useful from the chemical point of view are those by Emeléus[137] and Haissinsky.[135]

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SECTION XLV

THE HALOGEN PRODUCTS OF THE FISSION OF THE HEAVY ELEMENTS

By G. R. MARTIN

Bromine and iodine are the only halogens which are found to a significant extent amongst the products of the nuclear fission of the heavy elements; these two halogens, however, occur in substantial yields in almost all the cases so far examined. In fact, within a few weeks of the announcement of the discovery of fission by Hahn and Strassmann[1], it had been demonstrated by Abelson and, independently, by Feather and Bretscher that the X-radiation emitted by the 3-day activity present in the 'eka-platinum' fraction of the 'transuranic elements' formed in the neutron irradiation of uranium, and previously attributed to the L X-rays of a transuranic element, was actually the K X-radiation of iodine. This was shown, in the first place, by critical absorption studies, but the same authors also showed that the 3-day body followed the chemical reactions of tellurium, whilst its 2·5 hour daughter was carried quantitatively on silver iodide precipitates. Bretscher and Cook also demonstrated that these radioactive halogen nuclides could be collected on a plate held near a neutron-irradiated layer of uranium, utilizing the energetic recoil to which, as products of so exoergic a reaction, they were subject.[2,3,4,5]

Isotopes of iodine and, to a lesser extent, of bromine played a prominent part in the early investigations of the fission of uranium and thorium, largely because these two elements were obtained in comparatively high yields and could be so easily isolated chemically and purified; a number of radioactive isotopes of bromine and iodine were thus soon recognized as members of the decay chains which result from the fission process. Furthermore, the ease of purification and the sensitivity of detection of the radio-isotopes of iodine in particular has led to their use by several workers as a test for fissionability.[6,7] On the other hand, it may be noted that the variable valency of the halogens, and the absence of any rapid isotopic exchange process between certain of the valency states, makes quantitative work with these substances rather slower and more difficult than was at one time thought. On account of this difficulty of ensuring complete isotopic exchange between the active material (which may be formed originally in any of its possible valency states) and the added 'carrier', some of the earlier attempts at quantitative work on yields of the various halogen nuclides in fission have been called into question by later workers.[8,9,10,11]

The products of the fission of uranium, thorium and plutonium at moderate excitation energies tend to be 'neutron excess' nuclides, and therefore to decay predominantly by the emission of negative β-particles. With some lighter elements (lead and bismuth, for example) in which fission can be induced only by bombardment with particles of very high energy, no such generalization can be made; in these cases it appears that fission occurs only after the 'evaporation' of a substantial number of neutrons (thus increasing the 'fissionability parameter', Z^2/A, but decreasing the neutron/proton ratio), and the neutron excess of the ensuing fission products is by no means so marked. In such cases, a number of β-active bromine isotopes are found, but the iodine isotopes tend to be on the neutron-deficient side of stability, and thus to reach a stable product through the emission of positrons or through *K*-electron capture.[12,13,14,15] Tables I and II list the isotopes of bromine and iodine known to be produced in fission, with brief data on their nuclear properties and genetical relationships.

TABLE I. - BROMINE ISOTOPES FORMED IN FISSION

Nuclide	Half-life	Radiations	Parent nuclide	Daughter nuclide	References* to identification as fission product; genetic relationships, etc.
^{79}Br	stable	-	6·5 × 10^{4} yr. ^{79}Se	-	†
^{81}Br	stable	-	57 min. ^{81m}Se 17 min. ^{81}Se	-	†
^{82}Br	36·0 hr.	β,γ	shielded nuclide	stable ^{82}Kr	12,16
^{83}Br	2·4 hr.	β	67 sec. ^{83m}Se 25 min. ^{83}Se	stable ^{83}Kr	12,17-24,27
^{84}Br	33 min.	β,γ	~2 min. ^{84}Se	stable ^{84}Kr	19,23,25,26,28
^{85}Br	3·0 min.	β	either primary fission products or formed from very short lived selenium parents.	4·36 hr. ^{85m}Kr (80%) 9·4 yr. ^{85}Kr (20%)	18,28,29
‡					
^{87}Br	55·6 sec.	β,γ,n		stable ^{86}Kr + n (~3%) 78 min. ^{87}Kr (~97%)	18,29-33
^{88}Br	15·5 sec.	β		2·8 hr. ^{88}Kr	29
§$^{(89)}$Br	4·51 sec.	$(\beta),n$		2·8 hr. ^{88}Kr + n 2·6 min. ^{89}Kr	29,31-33

* References to other aspects of work with these nuclides, and more detailed information about radiation characteristics will be fouhd in Section XXXIX (page 963).

† Presumed product of β-decay of known isobaric selenium fission product.

‡ Either ^{86}Br is very short-lived, or the stable ^{86}Kr is formed directly as a primary fission product.

§ The parentheses indicate that the mass assignment is not certain.

ASSIGNMENT OF NUCLEAR MASSES

Many of the nuclides involved are known to be formed in other nuclear reactions, and there is then usually little difficulty in making mass assignments by conventional means. In some cases this is not possible, and the assignment of a mass number to a particular activity must be made by methods such as the following which are, to some extent, peculiar to fission product studies.

(*a*) By observation of the growth and decay of the activities of the halogens and of the neighbouring nuclides genetically related to them, it is possible to make fairly unequivocal assignments to radioactive decay chains. The decay processes involved in fission product transformations (if one excludes the rather rare branching mode of decay involving the spontaneous emission of a neutron) do not give rise to any change of mass number, and the identification of any one member of the chain establishes the mass assignment of the chain as a whole. For example, the identification of the 22 hr. iodine as the progenitor of the 5·3 d. ^{133}Xe (which can be prepared by a number of alternative routes) enables this iodine isotope (and its 60 min. tellurium precursor) to be assigned to this mass number.[23,29,42,48,51,52] Such identifications can often be greatly facilitated by mass-spectrographic separation of the material (or of something genetically related thereto) prior to radiochemical examination.[53,54,55]

(*b*) In general, the fission of a given nuclide under given conditions (e.g. ^{235}U with thermal neutrons) gives for the products a smooth relationship between mass number and yield. Provided the yield can be measured, it usually

TABLE II. - IODINE ISOTOPES FORMED IN FISSION

Nuclide	Half-life	Radiations	Parent nuclide	Daughter nuclide	References* to identification as a fission product, genetic relationships, etc.
^{124}I	4 d.	K, β^+, γ	Primary products of high energy fission of bismuth and lead. Not found in fission at moderate energies	stable ^{124}Te	13,14,15
^{125}I	56 d.	K		stable ^{125}Te	
^{126}I	13·0 d.	β, γ		stable ^{126}Xe	
^{127}I	stable	-	90d. ^{127m}Te 9·3 hr. ^{127}Te	-	†
‡					
^{129}I	1·72 × 10^7 yr.	β, γ	32d. ^{129m}Te 72 min. ^{129}Te	stable ^{129}Xe	34,35,36
‡					
^{131}I	8·04 d.	β, γ	30 hr. ^{131m}Te 25 min. ^{131}Te	12 d. ^{131m}Xe (1%) stable ^{131}Xe (99%)	37,38
^{132}I	2·4 hr.	β, γ	77 hr. ^{132}Te	stable ^{132}Xe	2,3,4,12,37,39,46
^{133}I	22 hr.	β, γ	60 min. ^{133}Te	2·30 d. ^{133m}Xe 5·27 d. ^{133}Xe	27,37,39-46
^{134}I	51 min.	β, γ	43 min. ^{134}Te	stable ^{134}Xe	27,37,39,45,46
^{135}I	6·7 hr.	β, γ	either primary fission products or formed from very short lived tellurium parents.	15 min. ^{135m}Xe (~10%) 9·2 hr. ^{135}Xe (~90%)	9,40-42,47-49
^{136}I	86 sec.	β, γ		stable ^{136}Xe	18,50
^{137}I	22 sec.	β, n		stable ^{136}Xe + n (~6%) 3·9 min. ^{137}Xe (~94%)	18,29-32
^{138}I	5·9 sec.	β		17 min. ^{138}Xe	29
^{139}I	2·7 sec.	β		41 sec. ^{139}Xe	29

* References to other aspects of work with these nuclides, and more detailed information about radiation characteristics, will be found in Section XXXIX (page 963).

† Presumed product of β-decay of known isobaric tellurium fission product.

‡ ^{128}I and ^{130}I (which have not been reported in fission) are shielded by stable ^{128}Te and ^{130}Te, respectively.

enables the mass number of the product to be fixed, at the worst within about 2 mass units, if not quite certainly. This is especially a valuable method for the halogens, since Thode and his collaborators have made accurate measurements of the yields of the stable (or long-lived) krypton and xenon isotopes into which a number of bromine and iodine fission products decay; in this way, for example, the 54 min. iodine has been assigned[35] to mass 134.

(*c*) Considerations of conservation of momentum in the process of fission dictate a relationship between the distribution of mass between the two fragments and the distribution between them of the available kinetic energy. As is to be expected, this leads to a more or less smooth relationship between mass number and range of the fragment and, although in practice this is somewhat blurred by the straggling of the range of fragments, it is a useful method for making at least rough mass assignments. It has been used especially with the short-lived bodies responsible for the emission of the 'delayed' neutrons in fission (*q.v.*);[33,56] but can be quite generally applied.[24]

HALF-LIFE DETERMINATION

For many of the halogen activities involved, the half-lives are of such a magnitude that the normal method of plotting and resolution of decay curves can be used. Some ingenuity is frequently needed to obtain measurements on one nuclide without the confusion caused by the presence of other (particularly isotopic) activities, but this can often be achieved through the judicious timing of irradiations and chemical separations, or by the measurement of decay curves through suitable absorbing screens.[57]

The half-life of ^{129}I is too long for measurement in this way, and the value has been deduced from the disintegration constant obtained by absolute counting of a sample which was subsequently analyzed volumetrically for total iodine and mass-spectrometrically to determine the ^{129}I content.[56,58] Several isotopes of bromine and iodine have half-lives too short for convenient measurement by the normal plotting of decay curves, although the speed with which silver halide precipitations can be made has enabled direct decay measurements to be made even on the 4·51 sec. bromine isotope tentatively assigned[33] to mass 89. For some of the very short-lived bodies, a method based on the subsequent measurement of the amount of suitable longer-lived daughter substance retained in silver halide precipitates formed at various times after the end of the irradiation has been utilized. Here again the ease and speed with which silver halides can be isolated is of great service, although the method depends on the assumed constancy of the 'setting time' for these precipitates and some inaccuracy is introduced by slight variations in the conditions of precipitation.[29,59]

FISSION YIELDS

The fission yield for a given nuclide (*i.e.* the fraction of fissions which give rise to it) can be split into two parts: that formed through the decay of an earlier member of the same chain, and that formed directly in the fission act (the 'independent yield'). In practice, it is frequently rather difficult to make measurements accurately enough to draw this distinction unless the independent yield concerned is a substantial fraction of the total yield and the half-lives of the relevant nuclides are suitably related. It is, moreover, difficult to distinguish experimentally between the direct production of a nuclide in fission and its formation through a short-lived (excited) isomer of an earlier member of the decay chain. An example of this state of affairs is provided by the discovery of a short-lived (67 sec.) isomeric state of ^{83}Se, which explains the apparently anomalous independent yield of ^{83}Br observed in the slow-neutron induced fission of ^{235}U.[22]

Reliable information on independent yields can be obtained for a few 'shielded' nuclides, whose formation through β-decay of an earlier member of the decay chain is prevented by intervention of a stable neighbour. Thus ^{82}Br, which is shielded by the stable ^{82}Se, has been found, for example, to be produced in the slow-neutron fission of ^{235}U in a yield of $3{\cdot}5 \times 10^{-5}$%, as against an expected value for this mass (deduced from the smoothed curve of yield as a function of mass number) of 0·3%; the balance is, presumably, made up by the formation of the stable ^{82}Se, or of a short-lived (and as yet unreported) ^{82}As.[16,60] Independent yields have also been reported[60,61] for ^{133}I and ^{134}I.

Numerous workers have made measurements of the yields of a number of halogen fission products in the course of extensive investigations of the yield/mass-number relationships for several fissile materials.[9,16,20,22,26,44,47,50,54,61-75] Although these relationships are now, in general, well enough established, measurements have not been made for all the individual nuclides concerned, and even those individual results which are available are subject to a substantial uncertainty arising essentially from the errors involved in making the necessary absolute measurements of the activities produced. Table III lists the percentage yields for the fission chains in which bromine or iodine isotopes appear, taken from the smooth curves of fission yield as a function of mass;[64,65,66,68,76-80] the experimental measurements are for the most part in agreement with these values (within the experimental error), although there are a few noteworthy deviations which are commented on on page 1084.

TABLE III. - FISSION YIELDS FOR HALOGEN CHAINS[9,47,50,55,74,75,77]

Mass no.	Known members of decay chain.	Cumulative yields from smoothed curve		Measured yields of halogen members in ^{235}U fission
		^{235}U	^{239}Pu	
79	Se→*Br*	0·05	0·01	-
81	Se^{m} ↘ Se→*Br* As ↗	0·14	0.03	-
82	*Se* *Br→*Kr*	0·30	0·05	3·5 × 10^{-5}
83	Se^{m} ↘ Br→Kr^{m}→*Kr* Se ↗	0·47	0·15	0·48, 0·35
84	Se→Br→*Kr*	0·70	0·22	0·65
85	↗Kr^{m}↘ Br Rb ↘Kr↗	1·20	0·40	-
87	↗*n* Br→Kr→Rb→*Sr*	2·60	0·90	-
88	Br→Kr→Rb→*Sr*	3·8	1·6	-
(89)	↗*n* Br→Kr→Rb→Sr→*Y*	4·9	1·9	-
127	↗Te^{m} Sb ↘Te↗*I*	0·15	0·38	-
129	↗Te^{m} Sb ↓ ↘Te↗I→*Xe*	0·90	1·6	-
131	Te^{m} ↗Xe^{m} ↓ I ↓ Te↗ ↘*Xe*	2·80	3·7	2·8, 1·7, 3·0
132	Sb→Te→I→*Xe*	3·4	4·8	4·9
133	Te→I→Xe→*Cs*	4·7	5·0	4·6, 3·8, 5·2
134	Te→I→*Xe*	5·9	5·3	5·7, 7·8
135	↗Xe^{m} I ↓ Cs-*Ba* ↘Xe↗	6·0	5·6	5·6, 4·3
136	I-*Xe* *Cs-*Ba*	6·1	5·8	3·1
137	↗*n* ↗Ba^{m} I-Xe-Cs ↓ ↘*Ba*	6·2	5·9	-
138	I-Xe-Cs-*Ba*	6·2	5·9	-
139	I-Xe-Cs-Ba-*La*	6·1	5·9	-

Stable nuclides are italicized; shielded nuclides are indicated by an asterisk. Independent yields of the order 1% have been reported for the nuclides ^{133}I and ^{134}I.[60,61] In this region the yield curve is appreciably distorted by 'closed shell' influences, and the values deduced from the smoothed curve are probably too low.

Various halogen isotopes have been found as products of the fission of uranium or of thorium by protons, deuterons and alpha-particles of moderate energies (~5-30 MeV.),[81-84] and it seems probable that the yields in these cases, although mostly without experimental confirmation, do not differ greatly from those found for the corresponding neutron-induced fissions.

In the fission of the heavy elements by particles of very high energy (~100 MeV.) a yield curve with a single central maximum is found, as mentioned above; Table IV lists the available information on yields in the fission of bismuth with deuterons of 190 MeV.[12,14,15,85,86]

DELAYED NEUTRON EMISSION AND EVIDENCE FOR NUCLEAR SHELL STRUCTURE

Shortly after the discovery[87] of the existence of 'secondary' neutrons as products of the fission of ^{235}U, it was noticed that some of these secondary particles were emitted not instantaneously (as most were) but only after a measurable delay.[30,88,89,90] The time-distribution of these delayed neutrons

TABLE IV. - YIELDS OF HALOGENS IN FISSION OF BISMUTH BY 190 MeV. DEUTERONS.[15]

Mass number.	Predicted		Measured		Total yield found for chain.‡
	primary product	yield %	Product	yield %	
82	Se, Br	3·0	Br*	1·0▲	1·0▲
83	Br	3·2	Br	1·7▲	1·7▲
84	Br, Kr	3·4	Rb	0·3	0·3
86	Kr (stable)	-	-	-	-
124	Te, I	1·6	I* Sb(60 d.)	0·43 0·12	0·55
125	I	1·4	I	1·2	1·2
126	I	1·2	I*	0·11†	0·11†

* Shielded nuclides.

† Probably underestimated, since ^{126}I is now known to decay partly by orbital electron capture.

▲ Possibly low on account of chemical difficulties.

‡ This total necessarily omits the contribution from stable nuclides formed directly in fission.

TABLE V. - DELAYED NEUTRONS EMITTED IN FISSION

Half-life[32]	Assignment of activity	Range of fragment in aluminium (mg./cm^2).	Neutron energy (keV.)	Yields relative to 4·51 sec. activity			
				thermal neutron		14 Mev neutron	
				^{235}U	^{239}Pu	^{238}U	^{234}Th
		Refs: 33	32	32	94	98	98
55·6 sec.	^{87}Br	3·98 ± 0·06	250	0·12	0·11	0·18	0·45
22·0 sec.	^{137}I	3·21 ± 0·04	560	0·78	0·78	1·5	1·05
4·51 sec.	$^{(89)}$Br	4·05 ± 0·03	430	1·00	1·00	1·00	1·00
1·52 sec.	mass 129-135	3·63 ± 0·12	620	1·13	0·81	2·0	0·63
0·43 sec.	-	-	420	0·40	-	0·64	0·17
Delayed neutrons as percentage of total				0·76	0·38		

can be represented by the sum of five exponentially decaying neutron activities, whose half-lives and neutron yields are shown in Table V.[32,91-99] There is some indication of a shorter-lived activity (half-life about 6 msec.),[32,95,96,100] and evidence for several longer-lived activities (3 min., 12min. and 120 min.); comparatively little is known about the latter, and their relative intensities are, in any case, very small (respectively 3× 10^{-5}, 1 × 10^{-7} and 5 × 10^{-9} of the 55·6 sec. activity).[101]

Three of these neutron activities have half-lives identical, within the experimental errors, with those of three of the halogen fission products (^{87}Br, 55·6 sec; ^{137}I, 22·0 sec; and $^{(89)}$Br, 4·51 sec.) and the phenomenon may conveniently be discussed here. The identity suggested by this correspondence between the respective half-lives has been confirmed by chemical separations: the 55·6 sec. and 4·51 sec. activities do, in fact, follow the chemistry of bromine whilst the 22·0 sec. activity has been shown to arise from an isotope of iodine.[31,33,59,102,103] The remaining two substantial contributors to the delayed neutron activity have not yet been identified, and the shortness of their half-lives would certainly make chemical identification difficult. Consideration of the range of the neutron-emitting fission fragments strongly suggests, however, that the 1·52 sec body has a mass number in the range 129 to 135.[33,56,104]

The assignments of the 55·6 sec. and 22 sec. activities provide interesting evidence in support of the theory which postulates the existence within the nucleus of completed 'shells' at neutron (or proton) numbers 50 and 82, two of the so-called 'magic numbers'.[105] It is suggested that the first additional neutron beyond these closed shells is bound abnormally loosely, with the result that neutron emission from nuclei with $N = 51$ or 83 occurs at comparatively low levels of excitation. ^{87}Br and ^{137}I, on undergoing β-decay, give rise to ^{87}Kr and ^{137}Xe respectively (both nuclei then having one neutron in excess of the respective complete shells), and it appears that some of the disintegrations lead to an excited state from which neutron emission (involving no potential barrier restrictions) occurs virtually instantaneously. The neutron emission is thus actually from an excited state of the daughter substance, ^{87m}Kr or ^{137m}Xe, but the half lives of these states are so short that the neutron emission appears to be associated with their 55·6 sec. ^{87}Br or 22 sec. ^{137}I precursors. The proposed decay schemes are shown in Fig. I.[31,102] The yields of delayed neutrons are substantially smaller than the fission yields for the chains concerned, and it is to be supposed that only a comparatively small fraction of the β-disintegrations leads to the neutron-emitting excited levels concerned.

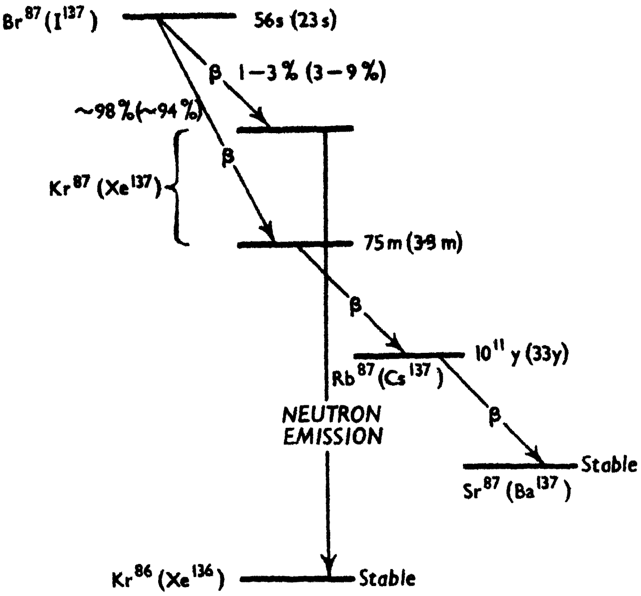

Fig. I. Decay scheme proposed to account for the 56 sec. and 23 sec. delayed neutron activities. Neutron emission is assumed to follow virtually instantaneously upon the β-transition.[31,102] The scheme proposed for the 23 sec. ^{137}I is shown in parentheses.

The spontaneous emission of delayed neutrons from fission fragments must produce some distortion of the otherwise generally smooth mass/yield curve, although this is a relatively minor effect. More significant is the apparent preference in the act of fission itself for the formation of 'closed shell' nuclei. ^{133}Xe, for example, has been shown to be formed to the extent of 1·25 times the yield to be expected from the smoothed yield curve;[87,104] it seems clear that this must represent an especially favoured mode of fission (presumably the primary product concerned is $^{133}_{51}$Sb, with $N = 82$), since it has been demonstrated that there is a corresponding anomaly in the region of masses (98–100) which would correspond to the fragment conjugate to one with mass 133. There is no other apparent explanation for the anomaly in the region of mass 100, and it must be regarded as strong evidence that this preference for the 82 neutron shell in the heavy fragment occurs actually in the initial act of fission rather than during evaporation processes subsequent to the primary split.[107] Similarly, ^{134}Xe appears in the slow neutron fission of ^{235}U with a yield about 1·35 times that expected, presumably on account of the especially favoured production of $^{134}_{52}$Te (also with $N = 82$) as a primary fission product.[67] ^{136}I (with $N = 83$) is, on the other hand, formed with a yield substantially lower than that expected.[50]

RADIOCHEMICAL PROCEDURES

Bromine and iodine, after conversion to the elementary form, can both be extracted from aqueous solution by distillation or by solvent partition, and the main chemical problem is to ensure that the active material is fully equilibrated with the added inactive carrier material before the extraction is performed. After extraction, further purification from non-halogen activities can easily be achieved by a succession of oxidation–reduction cycles, and bromine can be separated from iodine by utilizing the fact that iodide is oxidized by nitrous acid to elementary iodine whereas bromide is not affected. Alternatively, use can be made of the fact that hydroxylamine hydrochloride will reduce bromine to bromide without reducing iodine.

With neither element is there any appreciable exchange between the 'reduced' forms (X', OX' or X_2) and the more highly oxidized forms (XO_3', XO_4'), and some inaccuracy was probably introduced into earlier work by failure to ensure the recovery of material from the 5- or 7-valent conditions. For iodine, the most reliable method appears to be that involving the addition of iodide as carrier, followed by oxidation with alkaline hypochlorite; this reagent converts all the iodine into periodate, which can then, after acidification, be reduced by hydroxylamine hydrochloride to elementary iodine which is extracted and converted into a form suitable for measurement. Any bromine present is oxidized to bromate, which is reduced by hydroxylamine to bromide, extractable only after subsequent oxidation by, for example, permanganate; a clear separation of bromine and iodine activities can thus be achieved in a reliable quantitative manner.[10,11,108,109] Bromine, giving no stable ions containing the 7-valent element, poses fewer problems; it appears to be adequate to add bromate as carrier, followed by reduction to bromide and oxidation to elementary bromine for extraction.[110-113] When the fission products are formed in uranium metal, it may be assumed that they are necessarily present in the 'reduced' state, and a less involved procedure can be adopted.[114]

The bromine and iodine isotopes formed through the β-decay of selenium and tellurium will appear in various valency states, depending on the nature of the medium in which the disintegration occurs, the type and energy of the radiations involved, and the initial chemical form of the selenium or tellurium.[108,115-117] The problems of 'hot-atom chemistry' here involved are discussed in Section XLVII (see page 1106).

THE LONG-LIVED ^{129}I

It had long been suspected, on account of the apparent absence of any activity assignable to this nuclide, that ^{129}I would be a long-lived β-emitting substance. Natural iodine was known to contain less than 3 p.p.m. of this isotope,[118,119] which would argue against its half-life being greater than about 2×10^8 years; on the other hand, whilst ^{129}Sb and ^{129}Te were well-authenticated β-active fission products, a mass-spectrometric examination of the stable xenons formed in fission failed to disclose any ^{129}Xe,[54] suggesting that the half-life of ^{129}I was nevertheless very long compared with the period (about 1 year) which had elapsed between the irradiation of the uranium and the extraction of the xenon fission products from it.

An early investigation of a sample of fission product iodine (initially containing 40 curies of ^{131}I) disclosed a small residual activity, the amount of which would have corresponded to a half-life of about 3×10^9 years for ^{129}I if this was in fact responsible; probably, however, the counting apparatus used for this work would in any case have failed to detect the soft β-particles now known to be emitted by this isotope.[58] Later, Katcoff, using a radioactivation method of detection, demonstrated the presence of ^{129}I in fission product iodine, and estimated the half-life to be about 4×10^8 years. Further work has established a value of $(1{\cdot}72 \pm 0{\cdot}09) \times 10^7$ years, and has resulted in the characterization of the radiations from this isotope.[35,36]

It has been suggested that the radioactive decay of this nuclide may be responsible for the anomalous abundance of ^{129}Xe, which is one of the few exceptions to the empirical rule requiring the abundance of an odd-mass isotope to be less than that of either of its even-mass neighbours.[36,120] With a few further plausible assumptions, it has been deduced that the interval between the formation of the elements (when ^{129}I might be expected to have been roughly as abundant as the stable ^{127}I) and the formation of a stable atmosphere on the earth, is about $2{\cdot}7 \times 10^8$ years. Suess and Brown have suggested that this interval should be increased to about 4×10^8 years, and have further pointed out that the basis of the whole calculation is rendered uncertain by the fact that the even-mass neighbours of the are both to some extent 'shielded' by the stable nuclides ^{128}Te and ^{130}Te. The anomalous abundance of ^{129}Xe may be, in part at least, a result of abnormally low abundances for ^{128}Xe and ^{130}Xe.[121]

^{129}I is the longest-lived isotope so far identified in fission, and can be obtained in substantial quantities. This availability has facilitated the determination of various nuclear physical properties: the slow neutron capture cross-section (8×10^{-24} cm.^{2});[34,122] the nuclear spin ($^7\!/_2$);[123-125] the nuclear quadrupole moment ($-0{\cdot}47 \times 10^{-24}$ cm.^{2});[123,126] and the nuclear magnetic moment ($2{\cdot}6173 \pm 0{\cdot}0003\ \mu_N$).[124,127]

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Note. The following abbreviations, relating mainly to U.S. Atomic Energy Commission Reports, are employed:

AECD	Atomic Energy Commission Declassified
ANL	Argonne National Laboratory
BNL	Brookhaven National Laboratory
CC	Chicago Chemistry
LADC	Los Alamos Declassified
MDDC	Manhattan District Declassified
NNES	National Nuclear Energy Series (Vol. 9, Division 4, 'Radiochemical Studies: The Fission Products' Edited by C.D. Coryell and N. Sugarman, New York, 1951.)
NSA	Nuclear Science Abstracts
ORNL	Oak Ridge National Laboratory.

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SECTION XLVI

RADIATION CHEMISTRY OF THE HALOGENS.

By N. MILLER

The subject of 'Radiation Chemistry' may be defined as the study of the chemical effects produced by ionizing radiation, this being taken to include corpuscular radiation having energy sufficient to cause ionization, as well as all quanta of magnitude greater than about 50 eV. It is thus to be distinguished from 'radiochemistry', which may be defined as 'the study of the chemistry of bodies which are detected through their nuclear radiations', although in the past some confusion has existed between the two terms.[1]

The examination of radioactive materials and of the chemical effects of their radiations began to interest chemists after Becquerel had accidentally discovered the action of γ-rays from a salt of uranium on a photographic emulsion in 1896.[2] The study of reactions induced by electric discharges had, however, already been pursued to some extent, especially during the 19th. century.[3] During the early years of the 20th. century the two types of application of chemistry to the growing science of nuclear physics were pursued side by side, but gradually it became clear that more discoveries of fundamental importance to science were to be made at that time in radiochemistry. The rapid advances in our knowledge of both chemistry and physics consequent upon the proposal of the nuclear theory of the atom by Rutherford in 1911 transferred the interest of most workers to this subject, leaving radiation chemistry as rather an academic backwater. This it remained until the release of massive quantities of energy in the form of ionizing radiation became possible, as a consequence of the discovery of uranium fission in 1939.[4] Shortly after this, the chemical changes brought about by such large releases of energy in the form of ionizing radiation became of great technological importance. In the meantime the biological actions of ionizing radiation had been much studied by biologists and medical men, and these effects also had become of considerable practical significance. The consequence was a new and more determined attack on the fundamental principles of the subject in the years immediately following the 1939–45 war.

The pioneer workers in this field, such as the Curies themselves and their co-workers, and later Mund and his group at Louvain, Belgium and Lind and his school at Minnesota, had rather naturally become somewhat preoccupied with the chemical consequences of the most striking property of this type of radiation, namely the production of the ions themselves. Nevertheless it was clear at the time from studies on the electric discharge in gases that the ions produced were in this case accompanied by a considerable degree of electronic excitation of the molecules over and above that attributable to the neutralization of the charged species present.[5] This was shown most clearly by the fact that the energy required to release one ion pair in gases (about 30–35 eV.) was found to be considerably greater than the ionization potentials of the gases. Moreover, the growing science of photochemistry was revealing that species in a state of electronic excitation were of great importance in promoting chemical reactivity. The fusion of the older and the newer ideas began when Eyring, Hirschfelder, and Taylor in 1936[6] showed that the conversion of ortho- to para- hydrogen under the influence of the α-particles from radon, which had previously been examined by Capron,[7] could be explained with quite good quantitative agreement on the assumption that half the energy of the α-particles was consumed in producing ions and half in forming excited molecules which immediately dissociated into atoms. An experimental verification of the importance of electronic excitation was later achieved by Smith and Essex, who showed that the rate of decomposition of gaseous ammonia by α-rays was only slightly affected by the application of a saturation electric field which rapidly removed the ions from the reaction zone.[8]

Despite these advances, however, unravelling the detailed mechanism of chemical processes induced by ionizing radiation has proved to be a difficult matter. The most important cause contributing to this difficulty is the fact that the degradation of the energy of the impinging particles or quanta is achieved primarily within the electronic shells of the atoms, since the quanta concerned have energies far greater than the few eV. associated with chemical binding. Thus all atoms within the path of the beam are equally vulnerable to attack, irrespective of their states of chemical combination. No sooner does the concentration of the product molecule in any given reaction become appreciable than it too is attacked, either reversing the original process or promoting further consecutive processes. Naturally enough, therefore, modern experimentation is tending to concentrate more and more on the initial phases of reactions, and on the so-called 'indirect' processes in solutions where the concentration of solute is so low that it may be assumed that virtually all the energy of the radiation is being absorbed by solvent molecules.

It seems logical, in a modern approach to the radiation chemistry of the halogens with which this section is concerned, to begin by studying the elementary processes brought about by bombarding these elements, and their simpler compounds, with electrons, and thence to proceed to review such work as has been carried out on these materials using ionizing radiation.

ELECTRON IMPACT STUDIES ON THE HALOGENS AND HALOGEN HYDRIDES

Studies of this type have so far been made only on chlorine, bromine, iodine, and hydrogen chloride although reference is made in other work[9] to some studies by Blewett on impure bromine containing hydrogen bromide, leading to the conclusion that the chief positively-charged species produced in HBr is HBr^+.

(a). CHLORINE

Comparatively few electron impact studies have been carried out on chlorine, although the existence of chlorine atoms with as many as four positive charges, and also of Cl^- ions arising from electron capture, was demonstrated in an electric discharge in chlorine.[10] Electron attachment phenomena in this gas were further studied by Bradbury[11] and by Bailey and Healey.[12] According to the latter workers, attachment was a maximum for electrons of 1·5 volts energy, the process concerned being assumed to be $Cl_2 + e \longrightarrow Cl + Cl^-$. This is certainly possible energetically, as the electron affinity of the chlorine atom (3·7 V.,[13]: 3·76 V.,[14]) is higher than the dissociation energy of Cl_2(~2·8 eV.). Free chlorine atoms were detected in an electric discharge in chlorine,[15,16] and it was shown that their recombination required little activation energy on surfaces of a great many different materials, that on a quartz surface for instance having an activation energy of not more than a kilocalorie.[16]

An effect which must be borne in mind in any full interpretation of electron impact phenomena in chlorine is the so-called 'Joshi effect'. This is an experimentally observed lowering of the discharge current in an ozonizer discharge in chlorine when the chlorine is irradiated with blue or ultra-violet light.[17]

The effect, which is induced by light of wave-length 4120 – 4960 A.,[18] or more markedly by light of wave-length 2000 – 4000 A.,[19] is also shown, to a diminishing degree, by bromine[20] or iodine[21] vapour. If the effect is a genuine one taking place homogeneously in the gas phase, it must evidently be attributed to one or more of the following possible effects of light: (i) a decrease of average ionic velocity due to a change in the predominant ionic species produced, (ii) an increase in the energy necessary for an electron to form an ion pair, (iii) increased recombination of ions, or (iv) a decrease in the number of metastable species produced.[22] On the other hand, recent work tends to support the view that the effect is largely determined by the absorption of activated molecules on the walls of the vessel.[20,21]

(b). BROMINE

Positively Charged Species

A thorough mass-spectrographic study of electron impact processes in bromine was made by Blewett.[23] The chief species of positive ion were observed to be Br^+, with an appearance potential of 13·7 ± 0·5 V., and Br_2^+, appearing at 13·0 ± 0·5 V., in agreement with an earlier measurement which had given 12·8 V. for the ionization potential of Br_2.[24] Since the ionization potential of atomic bromine had been determined spectroscopically and found to be 11·8 V.,[25] it was evident that the Br^+ arose by the dissociation of the molecule-ion originally formed, viz. $Br_2^+ \rightarrow Br + Br^+$, the observed difference in energy between the appearance potential of Br^+ and the ionization potential of Br, 1·9 ± 0·5 V., corresponding to the dissociation energy of the bromine molecule. This figure is in good agreement with accepted values for this quantity. Since, however, no studies were made of the way in which the relative amounts of the different species formed varied with pressure, it was impossible to determine whether the Br_2^+ was produced by a primary or a secondary process.

The species Br^{++} appeared at 39·5 ± 1·0 V.; if this had been produced by a primary process $Br_2^{++} \rightarrow Br + Br^{++}$, Blewett pointed out, a study of the energetics of this reaction coupled with the known spectroscopic value of the ionization potential of Br^+ of 19·1 V.[26] would require the assumption that either the Br or the Br^{++} were left in an excited state having 6·7 V. excess energy.

Negatively Charged Species

These appeared in amounts similar to those of the positive ions. The quantity of Br^- rose to a maximum at 2·8 V. incident electron energy, and the Br^- ions formed carried 2·3 V. kinetic energy, as was shown by applying a retarding potential. Hence the electron affinity of the bromine atom could be calculated from the cycle: incident electron energy (2·8 V.) + electron affinity of Br atom = heat of dissociation of Br_2 (1·9 V.) + kinetic energy of fragments (2 × 2·3 V.). The resulting value, 3·8 ± 0·2 V., was in fair agreement with the values of 3·77 V.[27] and 3·55 V.[28] obtained from the Born-Haber cycle (cf. Sherman,[27]) and with that of Glockler and Calvin[29] (3·8 V.), obtained in 'space charge' experiments.[30]

With incident electrons of energy greater than 2·8 V., the amount of Br^- fell and then commenced to rise again at about 13·7V., the appearance potential of Br^+, providing some evidence for the occurrence of the process, $Br_2 \rightarrow Br^- + Br^+$. Under these conditions, Br_2^- was also formed to a smaller extent, but the shapes of the curves of the currents due to Br^- and Br_2^- as a function of electron energy were sensitive to the experimental conditions, indicating that some space charge effect was operative.

Neutral Species

Atomic bromine was identified spectroscopically by Schwab[31] in an electric discharge in bromine. Recombination of the bromine atoms was found to take place at every collision on the wall of the vessel, whether the surface of this were of copper, glass or picein wax.

(c) IODINE.

Positively Charged Species .

In 1923 W. A. Noyes, Jr., measured the minimum potential necessary to promote a luminous electric discharge in iodine.[32] The value obtained, 10·0 ± 0·2 V., was in fair agreement with the then current values of the ionization potential of the iodine molecule, viz. 10·1,[33] 9·4,[34] and 9·5 V.[35] A later mass spectrographic study by Hogness and Harkness,[36] showed that the species I^+ and I_2^+ both appeared at 9·3 V., but these values are all in conflict with the present accepted figure for the ionization potential of the iodine atom of 10·44 V., due to Murakawa.[37] The discrepancy between Murakawa's spectroscopic figure and those obtained in the mass-spectrographic work needs further experimental investigation. As the ionization potential of the iodine atom had at least been shown to be lower than that of the molecule,[38] it was evident that the I^+ was being produced by dissociation following ionization of the molecule, viz. $I_2 \rightarrow I_2^+ \rightarrow I + I^+$. The ratio of the amounts of the I_2^+ and I^+ formed proved to be a function of the pressure of the iodine vapour, indicating that a secondary process, probably $I^+ + I_2 \rightarrow I_2^+ + I$, was also occurring. Smaller amounts of I_3^+ were also present, the pressure dependence in this case being even greater. This species was attributed to the process $I_2^+ + I_2 \rightarrow I_3^+ + I$, as the alternative process, $I^+ + I_2 \rightarrow I_3^+$, was considered too exothermic to take place to any extent in the absence of a third body and failed, moreover, to explain the greater pressure dependence of I_3^+ formation.

The species I_2^{++} was detected in small amounts, with an appearance potential of 35·0 V., apparently by a primary process, as the pressure dependence in this case was small.

Negatively Charged Species

The singly charged ion I^- was found to be produced in amounts similar to that of the corresponding positive ion, by a primary process, presumably $I_2 + e \rightarrow I + I^-$. This process is energetically possible, as the electron affinity of the iodine atom ($\sim$3·2 V.)[39] is greater than the dissociation energy of the iodine molecule ($\sim$1·5 V.). In 1925 Mohler had studied the total current due to negative ions reaching a fixed cylindrical electrode from a concentric collimated beam of electrons in iodine vapour, and found that this was a maximum at zero incident electron energy, and increased again at critical potentials of 2·4, 4·6 and 8·4 V.[40] This was evidence for the production, by the electron beam, of excited iodine molecules having these energies, it being assumed that electrons which had been slowed down to a very low energy by the formation of such excited species would have a high probability of attachment to further iodine molecules. Later the existence of a maximum in negative ion formation at 2·5 V. electron energy was confirmed,[41] while Buchdahl found three maxima in all, at 0·4, 1·75 and 2·5 V., the first of which he attributed to the process $I_2 + e \rightarrow I + I^-$ with both atom and ion in the ground state, and the other two to electron capture in excited states of the iodine molecule to give the I^- ion in its ground state.[42]

I_2^- and I_3^- ions were observed by Hogness and Harkness in amounts corresponding to those of the positive ions; the secondary process $I^- + I_2 \rightarrow I_2^- + I$ and the tertiary process $I_2^- + I_2 \rightarrow I_3^- + I$ being supported.[36]

(d) HYDROGEN CHLORIDE.

The success of Born's theory of crystal lattices, by means of which it was possible, using simple thermochemical cycles, to compute such quantities as the ionization potentials ot metal atoms, the electron affinities of halogen atoms and the so-called grating energy of ionic crystals, i.e. the energy necessary to separate the constituent ions to infinity, had led in the early 1920's to considerable interest in the following cycle:

$$\begin{tikzcd}
\tfrac{1}{2}(H_2) + \tfrac{1}{2}(Cl_2) \arrow[rr, "Q\,(HCl)"] & & (HCl) \arrow[d, "X\,(HCl)"] \\
(H) + (Cl) \arrow[u, "\tfrac{1}{2}D\,(H_2)+\tfrac{1}{2}D\,(Cl_2)"] & & (H^+) + (Cl^-) \arrow[ll, "I\,(H)"', "-E\,(Cl)"]
\end{tikzcd}$$

Here all the entities are regarded as being ideal gases; Q (HCl) is the heat of formation of HCl; X (HCl), the heat of recombination of H^+ and Cl^-; D (H_2) and D (Cl_2) are the energies of dissociation ot the corresponding molecules; I (H) is the ionization potential of the hydrogen atom, and E (Cl), the electron affinity of the chlorine atom.

It had been widely assumed that the ionization potential of hydrogen chloride gas, as observed in electron impact studies where the product species were not identified, would give an indication of the quantity X (HCl) above;[43] but it was later shown by Barton in the first mass-spectrographic study of HCl that the first appearance potential, which he observed at 13·3 ± 1·5 V., corresponded to that of the HCl^+ ion, and not that of the H^+ and Cl^- ions implied in the above cycle.[44] Similar conclusions had been apparent from the absence of hydrogen lines in the spectrum of an electric discharge in hydrogen chloride vapour at potentials up to 120 V.[45] and from the observation that the currents of negative ions formed by electron impact in this gas were much lower than those of positive ions.[46]

Positively Charged Species

The first thorough study of the products of electron impact in hydrogen chloride was due to Nier and Hanson,[46] who quoted the following appearance potentials; HCl^+, 12·9 ± 0·2 V.; in good agreement with the spectroscopic value;[47] HCl^{2+}, 35·7 ± 1·0 V., H^+, 18·6 ± 0·3 and 28·4 ± 0·3 V.; Cl^+, 17·2 ± 0·5 and 21·2 ± 0·5 V.; Cl^{2+}, 45·7 ± 0·3 V.; and Cl^{3+}, ~ 160 V. Later work by Hanson[48] included a study of the kinetic energy of the fragments using retarding potentials, and in particular an examination of the kinetic energy of the H^+ ions produced as a function of the voltage of the incident electrons between 20 and 120 V. When the energy of the electrons exceeded 40 V., three peaks appeared in the plot of H^+ ion current against the kinetic energy of the ions, at about 4·8, 6·0 and 8·0 V. kinetic energy. These were attributed to the process $HCl^{++} \longrightarrow H^+ + Cl^+(^3P)$, the three peaks corresponding to the three J-values of the triplet-P state of Cl^+ formed. By studying the potentials necessary to form H^+ ions having definite kinetic energy and extrapolating the rosulting plot to zero kinetic energy, the appearance potential of H^+ ions having no kinetic energy was found to be 18·35 V., somewhat lower than the appearance potential recorded in the mass-spectrographic study just described. This indicated that in the mass-spectrographic work the H^+ ions observed had carried a small amount of kinetic energy. Attempts to correlate the data on the basis of the reaction $HCl^+ \longrightarrow H^+ + Cl(^2P_{3/2})$ or $(^2P_{1/2})$ led, however, to rather too high a value for the dissociation energy of the hydrogen chloride molecule.

By continuing the plots of the current due to ions carrying definite kinetic energy against the bombarding electron energy up to about 48 V., evidence was obtained for a further process corresponding to the second appearance potential for H^+ in the work already quoted, which was interpreted as $HCl^+ \rightarrow H^+ + Cl^*$ (11·6. V.). Further study of the data on the decomposition of HCl^+ led to a value of the dissociation energy in the process $HCl^+(^2\pi) \rightarrow H + Cl^+$ of 4·76 V.

Negatively Charged Species

These have been much less extensively studied. Barton,[44] Bradbury,[11] and Nier and Hanson[46] found that electrons of very low energy could be attached to HCl, the consequent process being assumed to be $HCl + e \rightarrow H + Cl^-$, as singly-charged chlorine ions had been identified by the latter authors in the products. The current due to negative ions was found by Hanson[47] to reach a peak when bombarding electrons of about 2·5 V. were used: by extrapolating the curve of negative ion current against bombarding electron energy, an onset potential of 0·4 V. for Cl^- ions was estimated. This led to a value of the electron affinity of the chlorine atom of about 4 V., in fair agreement with the values cited earlier.[13,14]

GAS-PHASE STUDIES OF THE RADIATION CHEMISTRY OF THE HALOGENS AND HALOGEN HYDRIDES.

(a) SYNTHESIS OF HYDROGEN CHLORIDE

The synthesis of hydrogen chloride from the elements is of course well known to be initiated by absorption of light of energy sufficient to dissociate the Cl_2 molecule, and to proceed thence by a chain process, the essential steps of which are:

$$Cl + H_2 \rightarrow HCl + H$$

$$H + Cl_2 \rightarrow HCl + Cl,$$

with chain termination by the process $Cl + Cl \rightarrow Cl_2$ at the wall, and some inhibition by the process $H + HCl \rightarrow H_2 + Cl$.[49] A similar synthesis can also be brought about by all types of ionizing radiation. Although one of the earliest experiments to be carried out on the chemical effects of *X*-radiation, that of von Hemptinne, led to a negative result regarding this reaction, this was largely due to ignorance in matters of dosimetry understandable at the time.[50] Somewhat later, positive results were obtained by Jorissen and Ringer using radium preparations in an experimental system such that the gaseous mixture was irradiated with the β-particles and the γ-rays from the preparation but not with the α-particles.[51] Rays from thin-walled bulbs containing radon were also shown by Taylor to be effective in promoting this reaction.[52] Careful studies of the reaction using similar alpha-ray sources were made by Porter, Bardwell, and Lind,[53] and the temperature coefficient of the process was found by Lind and Livingston to be similar to that of the photochemical process using light of wavelength 4537 A.[54] Rodebush and Klingelhoefer showed that the reaction could be induced by an electric discharge,[18] an observation later confirmed by Günther and Cohn,[55] while Günther and his colleagues also showed that the combination could be induced by *X*-rays,[56] and by a glow discharge in nitrogen containing small quantities of the two gases.[57]

As might be expected with a chain reaction of this type, having regard also to the somewhat primitive state of the science of radiation dosimetry at the time, agreement was not good between the quantitative values of the yields obtained in different laboratories. Expressing the yields in molecules of HCl formed per ion pair produced in the gaseous mixture by alpha-radiation, Taylor quoted a value of only 4000,[52] as compared with the photochemical yield of up to 10^6 molecules per quantum. Here the number of ion pairs formed by the alpha-radiation within the gas mixture was calculated by measuring the residual range of the RaC$'$ particles emerging from the thin-walled radon bulb normal to its surface, making corrections for the loss of energy in the wall of the bulb by the other particles involved and assuming the energy release per unit track length of the alpha-particle to be constant, which is, of course, only approximately true.[58] Porter et al., however, later showed that in the presence of water-vapour, which had not been rigidly excluded in Taylor's work, inhibitors were formed, possibly oxygen and chlorine dioxide; and that, by using well dried gases, ion pair yields apparently up to four times the quantum yield could be obtained.[52] The dosimetry in this case was also carried out by a procedure similar to that just described. Lind and Livingston found the apparent ion-pair yield very similar to the quantum yield using light of wave-length 4537 A.[54] These workers measured the doses administered by examining the rate of combination of hydrogen and oxygen brought about by the same radon bulbs, using this reaction as a gas-phase actinometer. The original calibration of this actinometer by Lind, however, in which gaseous radon was mixed with stoicheiometric hydrogen-oxygen mixtures, had also involved assumptions concerning the constancy of the energy release per unit track length and further assumptions concerning the spatial distribution of the decay products of the radon, which make the method little if at all superior to that of the preceding workers.[59] From the modern viewpoint, the only significant conclusions are that the ion-pair yield appears to be of the same order of magnitude as the quantum yield, and that the temperature coefficients of the two processes as induced by alpha-rays and light of wave-length 4537 A. are similar. Having regard to the equally unsatisfactory state of *X*-ray dosimetry at the time of the measurements, one can scarcely be more specific than this in a modern appraisal of the work of Günther and his colleagues, but it is worthy of note that in the work of Günther and Holm on the reaction as induced in the glow discharge in nitrogen, the ion pair yield was independent of the relative flow rates of the nitrogen and the gaseous mixture.[57] In these measurements, which included comparisons with photochemically-induced processes, Günther and Holm estimated that each ion pair formed in nitrogen resulted in the initiation of about two chains.

Hydrogen chloride gas freed from oxygen and in the absence of surfaces, such as mercury surfaces, which absorb chlorine atoms, has been shown to be inert to the electric discharge,[60] and it is a fairly safe assumption that in the absence of impurities capable of removing H or Cl atoms these merely recombine with no net decomposition of the HCl. Similar conclusions can also be drawn from earlier work on hydrogen fluoride.[61]

(b) SYNTHESIS AND DECOMPOSITION OF HYDROGEN BROMIDE

The synthesis of hydrogen bromide is another of the classic reactions of photochemistry. A mechanism exactly analogous to that given above for the photochemical synthesis of hydrogen chloride was postulated independently in 1919 by Christiansen,[62] Herzfeld,[63] and Polanyi,[64] and was later shown to be in accord with experimental observation by Bodenstein and Lutkemeyer.[65] The reaction proceeds more slowly at room temperature than the synthesis of hydrogen chloride, however, because the activation energy of the process $Br + H_2 \rightarrow HBr + H$ is higher than that of the corresponding process involving chlorine atoms.[66] An analogous reaction induced by alpha-rays was first noticed by Lind,[67] and an *X*-ray induced reaction was first reported by Günther and Leichter.[68] The alpha-ray induced reaction was later subjected to more detailed experimental examination by Gillerot,[69] Lind and Ogg,[70] Lind and Livingston,[71] and Ogg,[72] while the data of Lind and Livingston[71] were made the subject of a a theoretical study by Eyring, Hirschfelder, and Taylor.[9]

The chief experimental difficulty with the alpha-ray induced reaction as opposed to that induced thermally and photochemically is that the reverse reaction, the decomposition of HBr, cannot be neglected, even in the initial phase of the reaction. The ready decomposition of HBr in a spark discharge had indeed been noted many years earlier by Berthelot,[61] and similar decomposition in an ozonizer by Smits and Aten.[73] Moreover, in interpreting the results of the experiments we come face to face with one of the greatest difficulties in elucidating the mechanism of radiation-induced processes, viz., the entirely non-specific nature of the primary absorption. In this case, energy absorption takes place concurrently both in the hydrogen and in the bromine as well as in the HBr as soon as any appreciable amount of this appears. The situation is obviously much more complicated than in the thermal or photochemical reactions, where only one primary process, the dissociation of bromine molecules into atoms, is important.

These difficulties were first reported by Gillerot,[69] who noted that the yield of HBr per ion pair released in the gaseous mixture varied widely with the mol fraction of bromine. Lind and Livingston later made a detailed study of the effect of this variable, and found that the yield reached a maximum at about 0·03 mol fraction of bromine and then declined steadily as this mol fraction increased.[71] In this work the radon was mixed with the gases and dosimetry was carried out by the methods of Glockler and Heisig, in which corrections were made for the varying ion density along the alpha-particle tracks and for the distribution of the decay products on the walls.[89] The number of molecules of HBr formed per ion pair in the gas mixture was estimated at about 3·4 at its maximum value at 0·03 mol fraction of bromine; and at about 0·4 for an equimolar mixture, in fair agreement with Lind's earlier value of 0·54,[67] which was later confirmed by Ogg.[72] Günther and Leichter, studying the synthesis as induced by 40 kV. *X*-rays, found that the yield varied similarly with the mol fraction of bromine in this case, and quoted numerical values of 3·64 molecules per ion pair (34 eV.) in a mixture containing 8·9% Br_2, and 2·86 molecules per ion pair in another containing 26% Br_2.[68] The yield for the decomposition of HBr by alpha-particles was quoted by Lind and Livingston as 3·57 and 3·98 molecules per ion pair, in two experiments,[71] in fair agreement with Gillerot's earlier value of about 4·3[69] and with Ogg's later value of about 3.[72]

The findings of the alpha-ray work were interpreted by Lind and his colleagues on an ion cluster mechanism in which each ion was imagined to gather round it a cluster of molecules of the reactants, whereupon, on neutralization, energy equivalent to the ionization potential was released within these molecules. Such a mechanism would, however, gain little support now; much more likely to be correct is the assumption made in the later theoretical study by Eyring, Hirschfelder, and Taylor, that the most reactive entities produced on irradiating the gaseous mixture are H-atoms, by virtue of the fact that the reactions of such H-atoms with either Br_2 or HBr will be exothermic and require little activation energy, in contrast with the corresponding reactions of bromine atoms with H_2 or HBr, which are endothermic.[9] The situation is thus quite different from the photochemical reaction, where the rate-determining step is the dissociation of bromine and H-atoms are only produced by reaction of bromine atoms with H_2 molecules. By the action of alpha-rays, H-atoms will be produced continuously from both H_2 and HBr and will dominate the situation throughout. By examining the kinetic consequences of this assumption, Eyring, Hirschfelder and Taylor were able to explain most of the observations of Lind and Livingston quite satisfactorily if 6 atoms of H were assumed to be produced per positive ion formed in H_2 and 2 per positive ion in HBr. Eyring et al. did, however, point out the need for further work on this reaction before its mechanism could be fully elucidated.

(c) DECOMPOSITION AND SYNTHESIS OF HYDROGEN IODIDE

The decomposition of hydrogen iodide is again one of the classic photochemical reactions, and is now well recognized to be initiated by the direct dissociation of the HI molecule by light, followed by the processes:

$$H + HI \longrightarrow H_2 + I$$
$$I + I \longrightarrow I_2$$

Side-reactions involving atomic iodine have too high an activation energy to play an important part at room temperature, and the observed quantum yield of 2 is thus satisfactorily explained.[74]

A similar reaction is induced by all types of ionizing radiation. Decomposition of HI has been noted in a spark discharge[61] and in an ozonizer,[73] while the synthesis of HI in an ozonizer in a stream of hydrogen passed over solid iodine was observed by Warburg, who noted that the HI tended to decompose as soon as it was formed in the discharge.[75] The alpha-ray induced decomposition and synthesis of HI were first studied by Vandamme[76] and later by Brattain,[77] while Günther and his co-workers examined the decomposition under *X*-radiation.[78]

An interesting feature of the decomposition by both alpha- and *X*-radiation, on which all the workers agree, is that the yield per ion pair is independent of the pressure of the irradiated hydrogen iodide. Moreover, the agreement as to the numerical value of the alpha-ray yield is good, considering the status of radiation dosimetry at the time, Vandamme obtaining an average value of 8·2 molecules HI decomposed per ion pair formed, and Brattain about 6. The *X*-ray yield of Günther and Leichter, subject to even greater dosimetric uncertainties, was also about 8. These results are all consistent with the view that the hydrogen atoms are the more important reactive entities produced on irradiation. Later work by Günther, Leichter, and Pfyl showed that liquid and solid hydrogen iodide were much less sensitive to radiation, the yield being about one fifth of that observed in the gaseous phase.[78]

In Brattain's study of the synthesis of hydrogen iodide it was evident that the process resembled the synthesis of hydrogen bromide in that the yield of HI observed per ion pair was sensitive to changes in the composition of the gaseous mixture, although it was claimed that the results could not be explained on the basis of mechanism similar to that propounded by Eyring et al. for HBr.[9] A maximum value of the yield for the synthesis, at a mol fraction of iodine of 0·12, had also been noted earlier by Vandamme.

STUDIES ON HALOGEN-CONTAINING IONS IN AQUEOUS SOLUTION

These studies are all concerned with solute reactions induced in dilute aqueous solutions by ionizing radiation, and they can all therefore be described as studies of the 'indirect' action of such radiation on water, in the molecules of which almost all the energy of the radiation is dissipated. A general study of this subject is thus obviously more appropriate to the section of this work dealing with water, and no attempt is made here to include a comprehensive study by way of introduction. In the meantime the reader is referred to reviews such as those of Lea,[79] Allen,[80] and Dainton.[81] In brief it can be said here that it is now generally accepted that the predominant action of ionizing radiation on water is to set free hydrogen atoms and hydroxyl radicals either by the break-up of ionized molecules and the capture of the resultant electrons by other water molecules, or by direct dissociation of the water molecules in excitation processes. These atoms and radicals, being highly reactive, are considered to be responsible for the changes induced in solutes dissolved in the water.

The oxidation of air-free solutions of potassium iodide with evolution of iodine under the action of dissolved radium or radon was first noticed by Lind,[67] while the prolonged investigation of the action of radium γ-rays on many different materials, made by Kailan in the years 1911 – 1939, included examinations of such action on solutions of the halides of the alkalis and alkaline earths in air-saturated water. In all cases except that of potassium chloride, Kailan found that oxidation took place with evolution of the halogen, and proved to be more rapid in acid solution.[82] Strontium and barium iodides appeared to be more readily decomposed than the alkali metal salts, and magnesium iodide was more readily decomposed in alcoholic solution than in aqueous solution.[83] The rate at which the halogen was evolved from potassium bromide increased with increasing concentration of bromide, but not proportionately to this concentration: likewise it increased as the strength of the radium sources was increased, but again not in direct proportion to this variable. Under otherwise identical conditions the rate of oxidation of potassium bromide was substantially less than that of potassium iodide, neglecting the action of any hydrogen peroxide possibly formed during irradiation. Studies of the irradiation of potassium iodide by X-rays were later made by Clark and Pickett, who found that the rate of oxidation was reduced in the absence of oxygen,[84] and by Woodard et al., who affirmed that the rate was the same in solutions of acetic acid and of sulphuric acid of the same pH, but higher in nitric acid solution.[85] Woodard et al. also noted that the rate varied for the three salts, lithium, potassium and barium iodide, and confirmed Kailan's observation that the rate of oxidation did not increase proportionately to the rate of energy release in solutions containing 6·5% LiI, 10% KI or 25% KI in 0·05N-sulphuric acid. Fricke and Hart observed that iodide and bromide ion, in concentrations of 0·01 to 1×10^{-3}M., increased the rate of appearance of hydrogen peroxide in irradiated gas-free water or dilute sulphuric acid of pH 3.[86] In alkaline solution (NaOH, pH 11), Fricke and Hart found that hydrogen peroxide did not appear, but instead the equivalent quantity of oxygen, while such effects, according to these workers, were not brought about by chloride ions.

These observations on the catalysis of hydrogen peroxide production by traces of bromide and iodide ion, later confirmed by Haissinsky and Lefort,[87] were quoted by Allen in the statement of his theory of the decomposition of water by ionizing radiation, in which the radicals H and OH, considered to be formed by the decomposition of water molecules, were assumed to have different fates depending on whether or not they were formed in regions of intense local energy release such as the ends of electron tracks or the main columns of alpha-ray tracks.[80] If they were formed in such regions it was considered by Allen to be likely that some would recombine in like pairs to give H_2 and H_2O_2 molecules. These molecules would then diffuse out into the body of the solution, where, in the absence of any other solutes, they would be consumed in chain reactions initiated by other radicals, which, not having been formed in zones of high energy release, were free to attack them. The overall decomposition of pure water into hydrogen and hydrogen peroxide would thus be small, in agreement with observation. If, however, solutes such as halide ions were present, they would be expected to remove radicals by electron transfer processes such as $OH + Br^- \rightarrow Br + OH^-$ followed by $H + Br \rightarrow H^+ + Br^-$, thus promoting the production of hydrogen and hydrogen peroxide, again in keeping with the experimental results. In deaerated solutions of Br^- and I^- Allen and Johnson did indeed find no oxidation of the halide ion, the only products being hydrogen, oxygen and a small amount of hydrogen peroxide.[88]

Haissinsky and Lefort, in further studies using X-rays, asserted that potassium iodide could ultimately be oxidized by such radiation in air-free solution at room temperature, and that iodine in potassium iodide solution could similarly be reduced; while in air-free 0·01N-sulphuric acid a steady state could eventually be reached starting with either solution when about 25% of the iodine was in the oxidized form. Quite different behaviour was noted when a potassium iodide solution was irradiated with alpha-particles from radon, the oxidation in air-free solution then proceeding linearly to completion. In dilute solutions of potassium iodide frozen and cooled to -190°C., the rate of oxidation by *X*-rays was much lower, but it decreased with concentration until at 1 M-KI it was almost the same as in 10^{-3} M. solution at room temperature.

It is perhaps worth noting that oxidation of potassium iodide in aerated aqueous solution can also be brought about by irradiation with high-frequency sound waves;[89] this phenomenon is attributed by most workers to electric discharges brought about within the gas-bubbles formed during the process of 'cavitation'.[90]

Although Kailan had not noted any production of chlorine on irradiation of potassium chloride solutions, evidence for the occurrence of the reaction $OH + Cl^- \rightarrow OH^- + Cl$ in aqueous solutions of chloride ion irradiated with γ-rays was obtained by Dewhurst, who found that the enhancement of the γ-ray yield for the oxidation of ferrous ions in air-saturated 0·8 N-sulphuric acid solution, which was brought about by traces of organic impurities, was suppressed by chloride ion in 10^{-3} M. concentration.[91] This enhancement was attributed to reactions between hydroxyl radicals and the organic molecules, with the consequent formation of organic free radicals which, in the presence of oxygen, formed organic peroxides, thus increasing the oxidation of ferrous ions. When chloride ions were present, the hydroxyl radicals were assumed to be removed by the reaction $OH + Cl^- \rightarrow OH^- + Cl$.

Little work has been carried out on aqueous solutions of halate or perhalate ions, but qualitative studies indicate that these species are all reduced by *X*- or γ-rays even in oxygen-containing solution. Such studies were made on solutions of potassium chlorate with radium γ-rays by Kailan, who found this salt was reduced to potassium chloride;[92] and on potassium iodate by Chamberlain, who found that free iodine appeared when solutions of this salt were irradiated with *X*-rays.[93] Chamberlain's results were confirmed by Haissinsky and Lefort, who found that potassium iodate solutions were reduced both by *X*-rays and by alpha-particles, with an initial *X*-ray yield one-fifth to one sixth of that for the oxidation of potassium iodide.[87]

SOLID PHASE STUDIES.

Comparatively little attention has been devoted to the chemical decomposition of solid salts containing halogen elements by ionizing radiation, although the physical changes brought about on irradiation of the alkali halides have been quite extensively studied, and will be examined in more detail later under the radiation chemistry of the alkali elements. In brief, these physical effects involve the migration of electrons within the lattice structure, with consequent changes in the transmission of visible or ultra-violet light and in other physical properties of the crystals.[94]

Meiler and Noyes studied the decomposition of solid potassium chlorate by electron bombardment and by irradiation with ultra-violet light in parallel experiments.[95] It was found that decomposition with evolution of oxygen resulted when electrons of energy greater than 22 V., or light of wave-length less than 2800 A., were used. The experiments with electrons may, according to the authors, have been somewhat affected by the build-up of surface charge on the salt during irradiation.

Observations of the decomposition of halates and perhalates by the radiation of a nuclear reactor were made incidentally in the course of studies of the excited atom chemistry of newly-formed ^{36}Cl,[96] and of newly-formed ^{82}Br.[97] The decomposition of potassium perchlorate crystals by 50 kV. *X*-rays was thoroughly studied by Heal.[98] The main products of the decomposition were chlorate and chloride ions, both appearing in reactions approximately of the first order; a calorimetric estimation of the yield led to the conclusion that 19 ± 2 eV. were required for the dissociation of a perchlorate ion. It was considered that the decomposition occurred in the main at surfaces and in lattice imperfections, the energy associated with the excitation of the ClO_4^- ions by the radiation being transferred along the lattice to these positions by an 'excitation' transfer process of the type postulated by Frenkel.[99] The resulting Cl^-, ClO_3^- and O_2 were then assumed to accumulate at these positions, until the crystals suddenly disintegrated, as was observed to occur. This hypothesis was supported by a sudden rapid increase in chloride ion formation at the moment of break-up of the crystals, which was attributed to the secondary formation of chloride ion from chlorate at the newly-formed surfaces, from which the evolved oxygen could readily escape.

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SECTION XLVII

THE EXCITED-ATOM CHEMISTRY OF THE HALOGENS.

By K. F. CHACKETT

This section deals with chemical reactions involving halogen atoms initiated by nuclear changes. Such interactions may be. for example, the formation of halogen-atom nuclei by radioactive decay processes, or by bombardment of nuclei with particles such as neutrons, protons, or helium ions, or with quantum radiations. In the special case of bromine, the initiating nuclear phenomenon may be the transition of bromine nuclei from an upper to a lower energy state, a process which occurs with the isotope of mass 80. Since in general (though not always) the energy liberated in nuclear reactions is many times that associated with ordinary chemical bonds, it is natural to expect bond rupture as one result of nuclear reactions. The newly-formed nuclei, together with any orbital electrons remaining associated with them, are known colloquially as 'hot-atoms', and their chemical reactions as 'hot-atom chemistry'. The term 'excited-atom' is perhaps preferable, if only because it does not necessarily imply that the original chemical bond is always broken by a recoil mechanism but suggests that other processes may be involved. This branch of chemistry is already well-developed for many elements besides the halogens, but in this development the halogens have probably played a greater part than any other group in the Periodic System, mainly because their usual chemical reactions are familar and they form well-defined series of both inorganic and organic compounds which are relatively easy to separate and identify.

Special mention should be made at the outset of the work of Szilard and Chalmers,[1] whose basic idea and experimental work on the bombardment of ethyl iodide with slow neutrons proved to be the foundation of this new field of research. Measurements have been made of the energies of the γ-rays emitted by several elements including chlorine, bromine, and iodine upon slow neutron capture. The upper limits are so high that the recoiling halogen atom has, in some cases, a kinetic energy many times greater than normal bond energies.[2] This affords an explanation of the effect observed by Szilard and Chalmers, namely, that a large proportion of the newly formed ^{128}I atoms are no longer in organic combination. The simple picture of recoil resulting from γ-ray emission causing rupture of chemical bonds is not, however, applicable to the cases where the halogen atom is combined with a very light atom.[3] It must also be pointed out that if the halogen nucleus loses its excitation energy by the emission of two or more γ-rays in random directions, the net recoil may be far less than if a single quantum only were emitted.

Since nuclear reactions are usually such rare phenomena, it is clear that the actual amount of chemical action arising therefrom will in general be extremely small, though exceptions to this rule are to be expected in the case of neutron reactions in the pile. Hence special methods are almost invariably necessary for the detection of reaction products. In practice this has always meant in the past relying on the fate of the halogen atoms being indicated by their own radioactivity resulting from the initial nuclear reaction. Thus the general method of identifying reaction products is to add to the system, after bombardment, a sample of pure inactive material identical in chemical nature with a suspected product, and, after suitable precautions to ensure equilibration, to separate out again a sample of this substance and to test whether, and if so to what extent, it carries with it the characteristic radiation of the halogen isotope involved. Obviously this method cannot be used if the reaction product sought has the property of exchanging its halogen with other possible chemical forms: for example, when working with aqueous media one could not expect to distinguish between molecular chlorine and chloride ion as reaction products since, owing to the rapidity of the exchange rate, the chlorine atoms, whatever their initial oxidation state (0 or -1) would be carried by either species.

In what follows, the excited-atom chemistry of the halogens is reviewed for fluorine, chlorine, bromine and iodine in turn. With each element the material has been arranged to deal so far as is convenient first with reactions involving inorganic compounds and then with those involving organic compounds. This arrangement necessitates the duplication of many references, since some authors have published papers concerning two or even three of the halogens, but it has the advantage of showing systematically what compounds have been studied. For a full account of the historical development of ideas concerning 'hot-atom' reactions, including reactions not involving the halogens, the reader should refer to a standard text on radiochemistry.[4,5]

FLUORINE

With fluorine, the only isotope which might conceivably be traced by the method outlined above is ^{18}F (half-life 112 min.). Although this isotope has been prepared in several ways there appear to be no reports of any of them being used in studies of the chemistry of the newly-formed atoms.[6] The isotope ^{20}F (12 seconds) is formed by the capture of slow neutrons in stable ^{19}F, in the form of CaF_2.[7] Its short half-life would, of course, make it extremely difficult to investigate chemically.

CHLORINE

Chemical reactions of the isotope ^{34}Cl (half-life 33 min.) have been studied. This nuclide is formed by proton bombardment of sulphur. Experiments in which solid sodium sulphate and sodium persulphate were bombarded showed that nearly 100% of the ^{34}Cl atoms may be co-precipitated with silver chloride from aqueous solutions of the targets. A barely detectable activity follows the chemistry of chlorate ion and perchlorate ion,[8] and even this may be accounted for by the slow exchange of chlorine between the valence states involved.[9] The irradiation of sodium chlorate by γ-rays also gives rise to ^{34}Cl, of which $91 \pm 2\%$ is found as chloride ion, $9 \pm 2\%$ being retained as chlorate ion, with negligible activities following chlorite ion or perchlorate ion chemistry.[10]

Slow neutron capture in the normal mixture of chlorine isotopes produces ^{36}Cl and ^{38}Cl. The former has a very long half-life (a figure of $4{\cdot}4 \times 10^5$ years has been given)[11] so that only in exceptional circumstances would the quantity produced be sufficient to permit its detection by radioactive means. However, experiments have been made in which solid sodium chlorate and solid sodium perchlorate were bombarded over a period of six months with neutrons from the Berkeley cyclotron. After dissolving the salts in water, it was found that a small but not negligible activity could be precipitated with silver chloride. That this was not the 38-minute ^{38}Cl isotope was shown by the apparent constancy of the activity with time.[12]

The other chlorine isotope made by slow neutron bombardment is ^{38}Cl having a half-life of 38 min., and it is this isotope which is involved in all the other researches mentioned here.

Irradiation of solid sodium chlorate with slow neutrons yields, after solution in water, between 70% and 90% of the induced activity in a form which may be co-precipitated with silver chloride.[13,14] That a small fraction of the active chlorine atoms in such an irradiation remains in an oxidized form seems to be indicated by experiments in which neutron-irradiated potassium chlorate was slowly decomposed by heating with oxalic acid and a little water. The chlorine dioxide evolved at first had a specific activity about ten times as great as that evolved towards the end of the reaction.[9]

Working with aqueous solutions as targets for slow-neutron irradiations, it is found that for sodium chlorate and sodium perchlorate solutions the proportion of active chlorine precipitable as silver chloride is very close to 100%.[13] The effect of pH has been investigated and it is found that under acid conditions the 'retention' of the activity by ClO_4^- is slightly greater than zero. This may be due to an increased exchange rate with the energetic ^{38}Cl atoms.[14]

The first organic chlorine compounds to be studied in this connection were chloroform and carbon tetrachloride. It is found that after slow neutron irradiation of chloroform, more than 90% of the active chlorine can be extracted by aqueous solutions containing inactive chloride ion. With carbon tetrachloride as target, the activity can be extracted also with an aqueous solution of a mild reducing agent (sodium thiosulphate), although under these conditions the percentage extracted is less, about 55%.[14,15]

In further work on these lines chlorobenzene was irradiated with slow neutrons, when it was shown that aqueous solutions containing chloride ion and sulphur dioxide could extract up to 50% of the active chlorine. Of the residual 50% of the activity retained in organic combination not all was present as chlorobenzene, for on adding dichlorobenzene to the target liquid and then recovering it by fractional distillation it was found that 15% of the total activity was present as dichlorobenzene.[16]

When ethylene dichloride is irradiated with slow neutrons active chlorine may be extracted with water (yield 60%), or by adsorption on activated charcoal (yield below 30%).[17,18]

There is good evidence that the proportion of molecules which dissociate as a result of neutron capture is higher than the proportion of active halogen eventually found in non-organic combination. This is shown by the fact that adding 4% of aniline to carbon tetrachloride and chlorobenzene before neutron irradiation causes a significant increase in the yield of active chlorine extractable into 5% hydrochloric acid or 5% sodium thiosulphate. Table I summarizes some typical experimental results.

TABLE I.- YIELD OF RADIOACTIVE CHLORINE FROM NEUTRON-IRRADIATED ORGANIC CHLORO-COMPOUNDS

Target	Added Substance	Extracting Agent	Mean % Extracted
Chlorobenzene	None Aniline	5% $Na_2S_2O_3$ 5% HCl	36 69
Carbon tetrachloride	None Aniline	5% $Na_2S_2O_3$ 5% HCl	55 88

The authors suggested that active chlorine atoms were the primary product in nearly every case, the fraction reappearing in organic combination representing recombination reactions. These would be competed with by reactions such as:

$$(1)\ R^{\bullet} + Cl + C_6H_5NH_2 \longrightarrow C_6H_5NH_2R^+ + Cl^-$$

where $R^{\bullet}$ denotes the molecular fragment resulting from the initial break-up of the RCl molecule. Alternatively, in some cases the γ-ray recoil might be sufficient to produce RCl molecules in a highly energetic state, when the reaction would be expressed as:

$$(2)\ RCl + C_6H_5NH_2 \longrightarrow C_6H_5NH_2R^+ + Cl^-$$

It would appear that there may well be little real distinction between these two reactions provided it is understood that the R and Cl in reaction (1) denote the original partners in one RCl molecule, as is probably true in most instances. In either case the postulated reactions constitute a mechanism whereby 'hot' halogen atoms, which would otherwise have re-entered organic combination, are in fact converted into halogen ions. These, of course, might still be highly energetic but are now given a 'second chance' to escape capture by a neighbouring molecule or radical and survive in an unbound state until various collision processes can reduce their energies to ordinary thermal levels.[15]

In 1947 Libby published a very important paper on the reactions of hot atoms formed by neutron activation; his ideas have become known as the 'physical impact theory' and with reference to organic halides may be summarized in the following way:

1. Breakdown of the halogen-containing molecule occurs in every case immediately on neutron capture.
2. The recoiling active atom has enough energy, E, initially to break through the surrounding 'cage' of molecules, so that the recombination of the fragments is negligible.
3. The active atom loses energy by the elastic collisions with surrounding atoms. Eventually, if by such processes its energy is reduced to a critical value ϵ, it can no longer move to a new site in the medium more quickly than corresponds to thermal agitation.
4. Since the hot halogen atoms are in general much heavier than other constituents of organic molecules, the energy loss at each collision will be quite small unless the hot atom strikes a bound halogen atom, which will usually be ejected from its molecule. The hot atom may still have energy greater than the bond energy ξ, in which case it will escape from the collision site and repeat the process elsewhere. Ultimately it will suffer a collision with a bound halogen atom, which leaves its energy less than ξ and in this case one of two things will happen. If the energy is still greater than ϵ, the atom can escape from the molecular fragments, but it can no longer eject another bound halogen atom, and so will probably not become organically bound. If the energy is less than ϵ it cannot escape the molecular fragments and will enter organic combination. The fraction of the whole activity eventually found in organic combination is therefore approximately $\frac{\epsilon}{\xi}$. This mechanism evidently accounts for the formation of radioactive molecules of the same type as the original target.
5. Molecules in which hydrogen atoms have been substituted by active halogens would, on this theory, be produced only when 'hot' atoms had been reduced by collisions to an epi-thermal region where

> the relatively slight energy drop caused by ejection of a hydrogen atom in a collision was yet sufficient to bring the energy below ϵ:
>
> $$\text{Hal}^* + C_nH_m\text{Hal} \longrightarrow C_nH_{m-1}\text{Hal}\,\text{Hal}^* + \text{H}$$
>
> In this region the energy of the hot atom must be of the order of normal bond energies, so that we may not speak of a truly elastic collision with the relevant hydrogen atom, but rather of a collision probably involving some excitation,with the molecule as a whole. This conception is necessary to explain the appreciable yields of radioactive di-substituted products.[19]

Libby's theory, later applied to the results of his experiments on propyl bromides (see page 1118) was put on a semi-quantitative basis by later workers;[20] and in a series of experiments a careful study was made of the reactions of ^{38}Cl formed by neutron capture in ^{37}Cl in various liquids. The yield of active chlorine as carbon tetrachloride was measured, as a function of the mole-fraction of carbon tetrachloride, in irradiated carbon tetrachloride-silicon tetrachloride mixtures. This yield is strictly proportional to the mole fraction over the entire range of composition, being zero at zero mole-fraction and 43% at unit mole-fraction of carbon tetrachloride. It was also shown that under the experimental conditions there is no appreciable exchange of radiochlorine between the two components of the mixture. This behaviour, however, is not reproduced in the system carbon tetrachloride-*cyclo*hexane as is shown by the figures in Table II (condensed from Miller and Dodson's paper[21]).

TABLE II.- YIELDS IN CARBON TETRACHLORIDE-*CYCLO*HEXANE SOLUTIONS

Mole-fraction Carbon tetrachloride	Radioactive Carbon tetrachloride	Radioactive Chloro-*cyclo*hexane
1·00	0·43	–
0·99	0·25	0·14
0·97	0·21	0·14
0·91	0·15	0·12
0·85	0·10	0·11
0·69	0·08	0·10
0·57	0·06	0·11
0·43	0·05	0·11
0·22	0·03	0·11
0·10	0·03	0·11
0·05	0·04	0·11

The constancy of the yield of radioactive chloro*cyclo*hexane is remarkable. A similar series of experiments with carbon tetrachloride-benzene mixtures gave the results shown in Table III (again condensed from the original paper).

In this case the constancy of the yield of radioactive chlorobenzene is remarkable, the variation among all the figures, after the first two, and their mean being almost entirely accounted for by statistical fluctuations in the counting rates obtained.

In an attempt to show that the initial state of combination of the chlorine had no effect on its fate after neutron capture, solutions of molecular chlorine in *cyclo*hexane and in benzene were also irradiated. The fraction of radiochlorine found in organic combination in the case of *cyclo*hexane was the same (0·2) at mole-fractions of chlorine of 0·003 and 0·022, but in the case of chlorine solutions in benzene there was a marked dependence of yield of radioactive chlorine in organic combination on mole-fraction, as shown in Table IV.

TABLE III.- YIELDS IN CARBON TETRACHLORIDE-BENZENE SOLUTIONS

Mole-fraction Carbon tetrachloride	Radioactive Carbon tetrachloride	Radioactive Chlorobenzene
1·00	0·43	–
0·99	0·30	0·12
0·97	0·27	0·16
0·92	0·23	0·22
0·90	0·22	0·24
0·82	0·17	0·21
0·65	0·12	0·22
0·53	0·12	0·22
0·38	0·10	0·20
0·29	0·08	0·18
0·23	0·06	0·20
0·15	0·07	0·20
0·08	0·06	0·18

TABLE IV.- TOTAL ORGANIC RETENTION IN CHLORINE-BENZENE SOLUTIONS

Mole-fraction Chlorine	Total organic retention
0·0010	0·20
0·0090	0·39
0·015	0·43
0·040	0·54

In a separate experiment it was found that the bulk of the radioactive yield in organic combination was not, however, as chlorobenzene but as higher-boiling fractions. Thus at a mole-fraction of chlorine of 0·015, the total organic 'retention' being 0·43, only 0·08 was present as chlorobenzene, and 0·35 remained inseparable from the products of photolysis of chlorine in benzene - essentially a mixture ranging in composition from $C_6H_6Cl_6$ to C_6Cl_{12}. This contrasts sharply with figures obtained for carbon tetrachloride solutions in benzene where, in one experiment with a mole-fraction of carbon tetrachloride of 0·65, the relative activities found as carbon tetrachloride, chlorobenzene, and higher boiling compounds were respectively 0·12 : 0·22 : 0·02.

A semi-quantitative explanation of all these phenomena is based partly on the 'physical impact theory', and partly on the conception that the preliminary reaction of all the hot chlorine atoms in solutions of chlorine or carbon tetrachloride in benzene or *cyclo*hexane is the formation of an activated complex with a hydrocarbon molecule. This latter hypothesis is necessary to explain why the yield of radioactive hydrocarbon halide is independent of the composition of the target, and also why small concentrations suffice to reduce drastically the yield of tagged carbon tetrachloride (since some at least of the complexes will decompose without making radioactive chlorine atoms available for substitution reactions with inactive organically bound chlorine atoms). This effect may be regarded in a sense as an extension of the explanation of the effect of aniline in reducing the organic yield of active halides, though in the present case we have no previous knowledge of the existence of the relevant complex.[21] Studies on the Szilard-Chalmers effect in hexachloroethane, both in the solid state and in solution in benzene and in carbon tetrachloride, have been reported.[22]

BROMINE

Hot radioactive bromine atoms have been produced by bombardment both with γ-radiations and with slow neutrons. Consideration must also be given to the chemical reactions of 18 minute ^{80}Br formed by internal transition of ^{80m}Br (4·4 hours half-life), and to the reactions of bromine atoms ^{83}Br and ^{84}Br formed by decay by β emission of selenium isotopes.

EXCITED BROMINE ATOMS FORMED BY γ-RAY BOMBARDMENT

Energetic γ-rays, for example those from a lithium target bombarded with protons, have been used to form the following isotopes of bromine[23]

(*a*) ^{78}Br, (6·4 minutes) formed by ^{79}Br (γ,n) ^{78}Br

(*b*) ^{80m}Br, (4·4 hours) formed by ^{81}Br (γ,n) ^{80m}Br

(*c*) ^{80}Br. (18 minutes) formed by ^{81}Br (γ,n) ^{80}Br.

In experiments with ethyl bromide as the target for the γ-rays, it has been shown that the concentration of the activity is possible by methods similar to those used in the normal Szilard–Chalmers process, namely extraction with aqueous media and co-precipitation with silver bromide. The active species are formed in the ratio $a : b : c = 1 : 3 : 2$ approximately.[24]

EXCITED BROMINE ATOMS FORMED BY NEUTRON BOMBARDMENT

Much more work has been done on the hot-atom chemistry of bromine following neutron capture. When sodium bromate is bombarded with slow neutrons and then dissolved in water, about 90% of the active bromine may be co-precipitated with silver bromide.[14] Work has recently been reported on this reaction using potassium bromate in the Oak Ridge pile.[25] With neutral or alkaline solutions of bromate as target, virtually all the active bromine may be co-precipitated with silver bromide, with or without previous extraction into carbon tetrachloride using ordinary bromine as carrier. With bromate solutions in nitric acid, however, the proportion of the total bromine precipitated with silver bromide falls to 20% presumably because the hot bromine atoms first formed react with nitrate ion to re-form bromate.[9]

Aqueous solutions of ammonium bromide and phenol irradiated with slow neutrons yield about 2% of the active bromine in organic combination.[26]

Most of the published work deals with the hot atom chemistry of bromine present in or reacting with organic compounds. One of the earliest studies was on the deposition of 18 minute ^{80}Br on metal foils immersed in neutron-irradiated organic bromine compounds including bromoform, ethyl bromide, ethylene dibromide and butyl bromide. No deposition occurred on smooth platinum, but definite activities were detected on copper and on silver. With bromoform the application of an electric field between two copper or silver plates (360 volts) increased the deposit of radioactive bromine on both plates; with ethyl bromide, ethylene dibromide and butyl bromide, the active deposit was confined entirely to the anode. In an experiment with bromobenzene, activity was found on the cathode, but to a smaller extent than on the anode. The presence of molecular bromine dissolved in the irradiated liquid reduced the efficiency of collection, presumably because radioactive ions exchanged with the inactive un-ionized form. It was shown that these observations hold whether electrolysis is carried out during or after the bombardment.[27] Other workers bombarded methylene dibromide and bromoform, in each case extracting inorganic active bromine with aqueous solutions of bromide ion and sulphur dioxide, and also estimating the yields of various organic bromo-compounds as reaction products, with the results given in Table V (see page 1113).

TABLE V.- PERCENTAGE OF TOTAL ACTIVITY CARRIED BY PRODUCTS OF NEUTRON IRRADIATION OF ORGANIC BROMO-COMPOUNDS

Substances irradiated	Percentage activity found in:-		
	Aqueous extract.	Original substance.	New product.
Methylene bromide	43	43	14 (bromoform)
Bromoform	34	47	19 (carbon tetrabromide)
Bromoacetic acid	78*		22 (methylene dibromide)

* Original substance remained in the aqueous extract

Various mixtures were also irradiated, each having only one constituent containing bromine, and it was shown that active bromine atoms were present in reaction products which could only be derived from the other constituent.[16] These results are shown in Table VI.

TABLE VI.- PERCENTAGE OF TOTAL ACTIVITY CARRIED BY PRODUCTS OF NEUTRON IRRADIATION OF PAIRS OF COMPOUNDS

Substances irradiated	Percentage activity in product.
Benzene + carbon tetrabromide (1:1)	Bromobenzene 15%
Phenol + methyl bromide (1:1)	Methyl bromide 6%; Bromobenzene 2%; Bromophenol 2%
Aniline hydrobromide	Bromobenzene 1%; Bromoaniline 2%.

The same workers observed that smaller yields of organically-bound bromine atoms are obtained if the target organic bromine compound, for example bromoform, is dissolved in a relatively large (20 : 1) volume of carbon disulphide.[16] This phenomenon is also observed with carbon tetrabromide in ethanol, the percentage of active bromine retained in the carbon tetrabromide molecule falling from 60 ± 5 in the pure state to 0 ± 2 at a mole percentage of 0·064.[9]

It has been shown that a large fraction of the active bromine formed by slow neutron bombardment of ethyl bromide may be extracted into water. The yield has been given as 60%; alternatively a yield of about 30% is obtainable by adsorbing the activity on charcoal.[17]

Experiments have been made on neutron irradiation of bromine as ethyl bromide and hydrogen bromide in the gas phase, using bombardments lasting only 45 minutes, and also lasting 12 hours. With the former the 18 minute ^{72}Br activity would have reached about 80% of its saturation, while the 4·4 hour ^{80m}Br would still be far from saturation, whereas with the latter both activities would be close to their saturation values. The results of the two series of experiments might therefore be expected to differ if the ^{80}Br and ^{80m}Br atoms underwent different reactions, but in fact such differences were scarcely appreciable. It was found that the proportion of active bromine found in organic combination was less than 3% of that formed. This indicates that practically all active bromine atoms formed in the ethyl bromide escape from their parent molecules. If, however, acetylene were present in the reaction mixture during bombardment (ethyl bromide 82mm., hydrogen bromide 5mm., acetylene 51mm.), the proportion rose to as much as 73%. This figure was not strongly dependent on the hydrogen bromide pressure between 2 mm. and 30 mm., nor was it affected very much by the admixture of 600 mm. pressure of hydrogen or of carbon dioxide during bombardment, or by the influence of an electrostatic field of 1000 volts applied across two electrodes within the irradiation vessel. The dependence of the yield of organically combined bromine on acetylene pressure was explained as follows.

Accepting that in all cases the activated bromine atoms are uncombined, one may expect an exchange reaction with HBr with velocity constant k_1,

$$HBr + Br^* \xrightarrow{k_1} HBr^* + Br \qquad \ldots\ldots (1)$$

and a reaction with acetylene to give a free radical, which reaction will be reversible,

$$C_2H_2 + Br^* \underset{k_3}{\overset{k_2}{\rightleftharpoons}} C_2H_2Br^* \qquad \ldots\ldots (2)$$

These free radicals may lead to production of stable organic molecules containing radiobromine by the reactions:

$$C_2H_2Br^* + HBr \xrightarrow{k_4} C_2H_2Br^*Br + H$$
$$\text{or} \quad C_2H_3Br^* + Br \qquad \ldots\ldots (3)$$

Assuming that the free radical concentration during bombardment is stationary, we have:

$$k_2[Br^*][C_2H_2] = k_3[C_2H_2Br^*] + k_4[C_2H_2Br^*][HBr]$$

The rate of production of stable organic molecules containing radiobromine, S^*, is

$$\frac{dS^*}{dt} = k_4[C_2H_2Br^*][HBr]$$

and of hydrogen bromide, HBr^*, is

$$\frac{dHBr^*}{dt} = k_1[Br^*][HBr]$$

The rate equations then lead to

$$\frac{S^*}{HBr^*} = \frac{k_2k_4[C_2H_2]}{k_1(k_3 + k_4[HBr])} \qquad \ldots\ldots (4)$$

Since it is found that the ratio of organic to non-organic bromine yield is almost independent of the pressure of hydrogen bromide, it must follow that $k_3 \gg k_4[HBr]$; neglecting this latter term and re-writing,

$$\frac{S^*}{HBr^*} = \frac{k_4[HBr]\,k_2[C_2H_2]}{k_3k_1[HBr]} \qquad \ldots\ldots (5)$$

we see that as the value of this expression is of the order of unity since $k_3 \gg k_4[HBr]$ it follows that $k_2[C_2H_2] \gg k_1[HBr]$.

In other words, the reaction of active bromine atoms with acetylene is much more probable than their reaction with hydrogen bromide. This, however, neglects the effect of the exchange reaction

$$C_2H_2Br^* + HBr \rightleftharpoons C_2H_2Br + HBr^* \qquad \ldots\ldots (6)$$

and consideration of this exchange leads to an equation

$$\frac{S^*}{HBr^*} = \frac{a[C_2H_2]}{b + c[C_2H_2]} \qquad \ldots\ldots (7)$$

which is shown to fit the experimental data as to dependence of the ratio of organically-bound to inorganically-bound radiobromine on acetylene pressure.

All this work depends on the assumption that every neutron capture leads to a free active bromine atom, which is not in fact always to be expected, since the HBr molecule may recoil as a whole. Owing, however, to the weakness of the neutron source used, it was not possible to detect any effect of non-rupture of the H–Br bonds.

Researches in which deuterium bromide was used instead of hydrogen bromide led to the same general conclusions, except that in all cases the yield of organically-bound bromine was significantly greater. This may be due to different rate-constants in the reactions, *e.g.* reaction (6) involving DBr instead of HBr.[28]

Further work with liquid-phase targets has been reported. The general plan of these experiments was to irradiate an organic halogen compound and then divide it into two or more portions. One was kept as a standard and its activity compared with that remaining in the others after they had been treated in various ways designed to remove non-organically-bound halogen. In the first series of experiments the effect of the presence of free halogen in the target during irradiation was investigated. The organic halide was given the following pretreatments before irradiation: (*a*) none, (*b*) shaking with aqueous sodium thiosulphate solution, (*c*) mixing with 1–3% of free halogen. After 20 minutes irradiation the liquid was divided into two portions and one was extracted with 5% aqueous thiosulphate to remove all free bromine and bromide. The results are given in Table VII.[15]

TABLE VII.- EFFECT OF FREE HALOGEN ON EXTRACTION OF RADIOACTIVE BROMINE

Target	Pre-treatment	% Extraction (mean)
Ethylene dibromide	*a*	51
	b	60
	c	69
Bromobenzene	*a*	31
	b	26
	c	30

In the second series of experiments the effect of different extracting agents was investigated and Table VIII summarizes the results.

TABLE VIII.- EFFICIENCY OF EXTRACTING AGENTS FOR RADIOACTIVE BROMINE

Target	Extracting Agent	Mean % extraction
Ethylene dibromide	Water	45
	5% HCl	43
	5% HNO_3	41
	5% H_2SO_4	40
	15% NaOH	51
	5% $Na_2S_2O_3$	51
	Zn, dust (2g.)	53
	Zn, coarse powder (2g.)	39
	Al foil	25
	Cu powder (2g.)	45
	Cu foil (2g. 55 cm^2)	18
	Ag foil (2g. 77 cm^2)	29

(Table continued on page 1116).

TABLE VIII. - *(continued.)*

Target	Extracting Agent	Mean % extraction
Bromobenzene	Water	20
	5% HCl	30
	15% NaOH	39
	5% $Na_2S_2O_3$	31
	Zn dust (2g.)	37
	Cu powder (2g.)	29

The effect of added bases such an aniline and phenol during irradiation was then studied, with the results given in Table IX.

TABLE IX.- EFFECT OF THE ADDITION OF ORGANIC BASES AND PHENOL ON THE EXTRACTION OF ACTIVE BROMINE

Target	Added substance	Extracting agent	Mean % extracted
Bromobenzene	None	5% HCl	30
	0·25% aniline	5% HCl	45
	1% aniline	5% HCl	63
	2% aniline	5% HCl	66
	4% aniline	5% HCl	76
	6% aniline	5% HCl	76
	4% aniline (added after irradiation)	5% HCl	35
Bromobenzene	None	15% NaOH	39
	4% phenol	15% NaOH	49
	4% dimethylaniline	5% HCl	72
	3% *m*-phenylenediamine	5% HCl	68
n-Butyl bromide	None	5% HCl	40
	4% aniline	5% HCl	74
	None	15% NaOH	38
	4% aniline	15% NaOH	57
Ethylene dibromide	None	5% HCl	46
	4% aniline	5% HCl	81
	4% phenylhydrazine	5% HCl	72
	4% diethylamine	5% HCl	68
	None	water	45
	4% aniline	water	71
	4% aniline	*	8
	None	5% H_2SO_4	47
	4% aniline	5% H_2SO_4	62

*Extracted with 5% HNO_3, the aqueous layer separated and made alkaline, and the aniline + bromoaniline extracted into 20 cc. inactive ethylene dibromide. The activity of this solution was then compared with the untreated portion of ethylene dibromide.

In all these experiments (except the last two on ethylene dibromide in Table IX), the irradiation time was so short (20 min.) that the activities detected were essentially due only to the 18 minute ^{80}Br isomer. The last experiments on the ethylene dibromide, which was bombarded overnight and allowed to stand for at least one hour for the 18 minute isomer to decay, refer to the 4·4 hour and 34 hour activities (^{80m}Br and ^{82}Br). In the experiment marked with an asterisk a measurement of the activity remaining in the target liquid was made, from which it was possible to calculate, by difference, the activity remaining in the aqueous phase. The latter activity was presumably due to Br since it was completely co-precipitated with silver bromide.

In the long-bombardment experiments a similar procedure was followed and, in addition, the activity of the water-soluble bromine fraction was determined by measurement after co-precipitation with silver bromide. The results of these experiments are given in Table X.

TABLE X.- DISTRIBUTION OF ACTIVE BROMINE IN ETHYLENE DIBROMIDE IRRADIATION

	18-min. activity	4·4-hr. + 34-hr. activity
Br* retained in $C_2H_4Br_2$	19	32
Br* substituted in aniline	8	9
Br* water-soluble	73 (by diff.)	59 (by diff.) 54 (by exp.)

Further experiments showed that the fraction of active bromine extracted in aqueous media was the same whether *n*-butyl bromide was irradiated at room temperature or at -80°C.

Finally some experiments were made on the extraction of activity from irradiated ethylene dibromide by metals (Table XI).

TABLE XI.- EXTRACTION OF 18 MINUTE ACTIVITY BY METALS

(1) Extraction by metal alone
(2) Extraction by metal followed by water extraction
(3) Extraction by metal alone (target saturated with HBr)
(4) Extraction by metal alone (4% aniline in target)

Metal	% Extraction			
	(1)	(2)	(3)	(4)
Zn, coarse powder	39	56	–	41
Al foil (400 cm^2)	25	53	–	10
Cu foil (55 cm^2)	18	50	7	[illegible]
Ag foil (77 cm^2)	29	48	0	27

In a typical experiment in which the active bromine formed by irradiation of 2,000 cc. of ethylene dibromide (+ 5% aniline) was extracted and converted into lithium bromide, the total bromine content of this salt was as little as 0·060 g. (found by titration), and it was calculated that the concentration factor (ratio of specific activities in the organic bromide and in the lithium bromide) was at least 30,000.[15]

Evidence has been found that, at any rate with ethylene dibromide as target, the inorganic yield varies with the time interval between the end of irradiation and the extraction process. Thus if this interval is made as short as possible, extraction with water removes only 35% of the active bromine from the organic liquid, but if the target liquid is allowed to stand in contact with pentane for 6 hours before extraction, the percentage extraction rises to 80.[29] That the radioactive bromine may undergo peculiar chemical reactions after the end of irradiation is suggested by a report that, if irradiated acetylene bromide is added to oleic acid and then removed again by distillation, the oleic acid is found to be brominated with a higher specific activity than the irradiated compound.[30] The deposition of ^{80m}Br and ^{80}Br on silver plates from irradiated organic bromides has been studied. The deposit is increased by applying an electric potential between pairs of plates; with ethylene dibromide more activity was collected on the cathode than on the anode, but the reverse is the case with bromobenzene.[31]

Experiments have been described in which mixtures of bromine and carbon tetrachloride, and also bromine and tetrachloroethylene, were irradiated both in the liquid phase and in the gaseous phase. The percentages of radioactive bromine found in organic combination in the liquid phase experiments were 24 and 37 respectively with very dilute solutions; in the gas phase the percentages were 1·9 and zero. A study was made of the yield of active bromine as a function of concentration of ordinary bromine in carbon tetrachloride. This fell approximately linearly from 24% in dilute solution to zero at 100 moles per cent. bromine.[32,50]

Other authors experimented with mixtures of hydrogen bromide and ethylene using a stronger neutron source than that available to earlier workers, which improved the counting statistics. They postulated the same kinetics for the HBr-C_2H_2 reaction as were mentioned above (see page 1114); with the same notation and also writing k_6 and k_7 for the neutron activation of hydrogen bromide and for the dissociation reaction

$$\mathrm{HBr} + n \xrightarrow{k_6} \mathrm{HBr}^*$$
$$\mathrm{HBr} + n \xrightarrow{k_7} \mathrm{H} + \mathrm{Br}^*$$

and denoting by (A) the partial pressure of ethylene, they derive

$$\frac{(\mathrm{A})}{\text{Org. Br}^*/\text{Inorg. Br}^*} = \{(k_1k_3/k_2k_4) + (k_1k_4 + k_1k_6)[\mathrm{HBr}]/k_2k_4\}\{1 + (k_6/k_7)\} + \{(k_5/k_4) + (k_6/k_7) + (k_5k_6/k_4k_7)\}(\mathrm{A})$$

so that with [HBr] constant, a plot of the left-hand side versus (A) should give a straight line with a positive slope and positive intercept on the ordinate. This prediction was in fact fairly well borne out by experimental results. It also appears that for ^{80}Br(18-min.) $k_6/k_7 = 0{\cdot}08$, whereas for ^{80m}Br(4·4-hour) k_6/k_7 is approximately zero. This is indicated by somewhat different distributions of the two activities between the organic and inorganic fractions.[33]

The conclusions regarding the value of k_6/k_7 appear to be supported by work on the deposition of both species of active bromine on gold electrodes immersed in neutron-irradiated ethyl bromide. It was found that the rate of deposition of ^{80}Br was rather lower than that expected, which might be accounted for if this species were not always produced as free atoms or ions. This work, however, is a little difficult to interpret.[34]

In most of the researches reviewed so far the active species investigated has been essentially the 4·4 hour ^{80m}Br isotope in equilibrium with its 18 minute daughter ^{80}Br. There may, however, be difficulties in the interpretation of results owing to this isomeric change. Other workers avoided these possible uncertainties by using a strong neutron source and basing all their results on the radioactivity of 34 hour ^{82}Br still present after the initially more strongly active ^{80}Br isomers had decayed. They irradiated both *n*- and *iso*-propyl bromides as pure liquids, as solids at -196°C., and as liquids containing 1g./100 cc. of bromine. The chemical nature of the active reaction products was established by the usual methods: extraction with aqueous bromide plus sulphur dioxide and addition of inactive organic bromides as carriers followed by fractional distillation. Experiments were also made to explore the effect of varying proportions of added bromine, of standing after irradiation, of the exclusion of air and of continuous extraction during irradiation. The results are given in Table XII, (see page 1119), where R is the percentage of activity not removable by aqueous extraction (i.e. the organic retention).

The authors applied the physical impact theory (reviewed briefly under Chlorine) to these results and made the following comments:

1. The yield of monobromo derivatives is essentially temperature-independent. This indicates a true excited reaction, i.e. the course of the substitution of an inactive atom by a radioactive atom is controlled entirely by the fact that the latter has an energy far above normal thermal values, so that it does not matter whether the reacting molecule is at a high or a low temperature.

TABLE XII. - HOT ATOM CHEMISTRY OF PROPYL BROMIDES

(*a*) Percentage yields of different reaction products.

Target	Chemical fraction	Irradiation conditions		
		Pure liquid 25°C.	Solid -195°C.	Solutions of bromine 1g./100cc.
n-Propyl bromide	*iso*Propyl bromide	12·0	11·3	4·0
	n-Propyl bromide	30·6	28·5	9·0
	1:2-Dibromopropane	3·8	20·2	8·4
	1:3-Dibromopropane	4·5	18·2	5·4
	R	50·0	78·2	28·8
*iso*Propyl bromide	*iso*Propyl bromide	10·0	11·2	7·9
	n-Propyl bromide	23·7	23·5	2·6
	1:2-Dibromopropane	3·8	20·0	6·7
	1:3-Dibromopropane	4·6	11·5	4·8
	R	42·1	66·0	21·4

(*b*) Effect of added bromine on retention: *iso*propyl bromide.

Concentration (g./100cc.)	3·5	1·0	0·35	0·035
Retention (%)	22·7	21·4	26·5	39·4

(*c*) Effect of standing in dim light for 24 hours after irradiation: *n*-propyl bromide with 0·7g. free bromine per 100cc.

Fraction	Intermediate	Delay
*iso*Propyl bromide	4·0	6·5
n-Propyl bromide	9·0	10·3
1:2-Dibromopropane	8·4	17·8
1:3-Dibromopropane	5·4	8·2
Water phase	28·8	42·8

(*d*) Effect of excluding air and of continuous extraction during irradiation of *n*-propyl bromide.

Fraction	Usual procedure	Air excluded	Continuous extraction
*iso*Propyl bromide	12·0	9·7	–
n-Propyl bromide	30·6	29·7	–
1:2-Dibromopropane	3·8	3·8	–
1:3-Dibromopropane	4·5	6·8	–
Water phase	50·0	51·0	50·0

2. *n*-Propyl and *iso*propyl isomers are formed in a ratio 2·4:1 from both normal and *iso*propyl mother molecules. This is taken to mean that the newly formed radioactive propyl bromide, whatever the initial configuration of the propyl radical, is energetic enough to be able to isomerize to an 'equilibrium' configuration appropriate to very high temperatures.

3. The yield of dibromo derivatives is much higher in the solids (-195°C.) than in the liquids (room temperature). This is an indication that in low temperature solids it is much more difficult than in liquids for an epithermal radioactive bromine atom to escape from any small region in the lattice. Hence there is increased probability of combination with a free radical from which it has ejected a hydrogen atom in a previous collision. From the existence of this effect, the authors predict that a rather sharp change in yield would be expected merely on cooling just through the melting point.

Refs. p. 1134

4. The retention of active bromine is greater in *n*-propyl than in *iso*propyl bromide. This may be due to more effective 'shielding' of the inactive bromine by the rest of the molecule in *iso*propyl bromide.

5. Addition of ordinary bromine to the irradiated liquid greatly reduces retention. This is presumably due to exchange between excited active bromine atoms and molecular bromine, a process which is likely to be more efficient than exchange with organically-bound bromine.

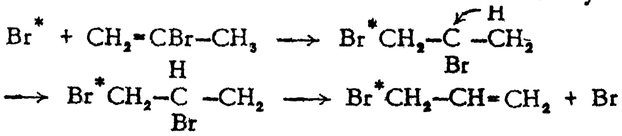
6. In the presence of bromine in the irradiated *iso*propyl bromide, there is inversion of the usual ratio of yield of the normal and *iso*-isomers which seems to have no simple explanation.

7. There is an increase in retention if the target liquid is kept in a dimly lit room for 24 hours fter irradiation before carrying out the extraction process. This may be due to a photochemical or oxygen-induced chain bromination of the alkyl halide.[35]

Electrical experiments relevant to the development of the theory of excited atom reactions were made by two workers who bombarded ethyl bromide in the gas phase at about 3 microns pressure with slow neutrons and observed the deposition of radioactive bromine on electrically charged plates. All three activities ^{80m}Br (4·4-hr.), ^{80}Br (18-min.) and ^{82}Br (34-hr.) were observed and the authors were able to infer the proportion of each species which was initially present as positively charged ions, the remainder being formed as neutral atoms. For the isotopic species mentioned, these proportions were 12%, 20% and 25% respectively.[36]

The direct production of organic bromides has been achieved using the uranium pile at the Atomic Energy Research Establishment, Harwell, as the neutron source. This made it possible to prepare very strong sources of many organic bromides, if necessary in carrier-free state, separations being achieved by distillation or by chromatography. Irradiation of mixtures of methyl bromide and benzene gave the following compounds, all tagged with ^{82}Br: methyl bromide, dibromoethane, bromobenzene and dibromobenzene. Carrier-free methyl bromide was best prepared by refluxing a mixture of acetic acid and 10% of dibromobenzene during irradiation, and sweeping out the methyl bromide continuously with a stream of air. After purification in a simple train the methyl bromide was finally frozen out into a cold trap; up to 50 millicuries could be so obtained with an unweighable amount of carrier material.[37]

Various bromo-olefines, such as $CH_2Br.CH{:}CH_2$, have been used as reagents for the capture of excited bromine atoms formed by neutron absorption in gaseous hydrogen bromide. With a pressure of this gas of 180 mm. and a pressure of olefinic bromide of from 1 to 25 mm., the yield of radioactive olefinic bromide was about 80%. In the liquid phase, using ethyl bromide and 1% vol./vol. bromo-olefine, yields varied between 25 and 50%. The authors suggest that the mechanism of this reaction is essentially an exchange:



$$\mathrm{Br^{*} + CH_2{=}CBr{-}CH_3 \longrightarrow Br^{*}CH_2{-}\overset{\curvearrowleft H}{\underset{Br}{C}}{-}CH_2}$$
$$\mathrm{\longrightarrow Br^{*}CH_2{-}\overset{H}{\underset{Br}{C}}{-}CH_2 \longrightarrow Br^{*}CH_2{-}CH{=}CH_2 + Br}$$

That such isomeric changes must occur is shown by the fact that when any one of the three isomeric bromopropenes is added (1%) to the bromobenzene and the mixture is neutron-irradiated, the activity distribution is approximately 22% 1-bromopropene, 3% 2-bromopropene, 75% 3-bromopropene.[38]

A study had been made of the effect of temperature on organic yield of radioactive bromine formed by (*n*,*γ*) reaction on dichlorodibromomethane, trichlorobromomethane, carbon tetrabromide, and solutions of bromine in carbon tetrachloride. Except with carbon tetrabromide there is an increase in yield as the temperature is lowered, in some cases with a probable discontinuity at the melting point. Actual figures are given in Table XIII.

TABLE XIII. - ORGANIC YIELD OF RADIOACTIVE BROMINE IN (n, γ) REACTIONS

Dichlorodibromo-methane		Trichlorobromo-methane		Carbon tetrabromide		Bromine in carbon tetrachloride	
Temp.°C.	% organic yield	Temp.°C.	% organic yield	Temp.°C.	% organic yield	Temp.°C.	% organic yield
32	40	25	40	100	88	25	27
22(m.p.)	—	−3	44	90(m.p.)	—	−23(m.p.)	—
0	75	−5(m.p.)	—	85	93	−190	50
		−6	58	25	93		
		−80	75				
		−190	72				

The effect of changes of phase and of temperature on the nature of the organic products was also studied and the results are given in Table XIV.[39]

TABLE XIV. - EFFECT OF CHANGES OF PHASE AND OF TEMPERATURE ON THE NATURE OF ORGANICALLY-COMBINED BROMINE FORMED BY (n, γ) REACTION ON TRICHLOROBROMOMETHANE

Chemical form	Organic yield %	
	25°C.	−80°C.
CCl_3Br	18	32
CCl_2Br_2	13	28
Higher boiling	8	15

EXCITED BROMINE ATOMS FORMED BY ISOMERIC TRANSITION

In the case of the bromine isotope of mass 80, formed by neutron absorption in the naturally occurring ^{79}Br, the situation is complicated by the phenomenon of nuclear isomerism because there exists, in addition to the ^{80}Br nucleus which decays by β-emission with a half-life of 18 minutes, a nucleus of higher energy content denoted by ^{80m}Br (m = metastable). This nucleus changes by what is known as 'isomeric transition', with the emission of quantum radiation, to the ^{80}Br nucleus, itself having a half-life of 4·4 hours. Physical evidence for the assignment of both these periods to the one nuclide has been presented.[40]

That the isomeric transition of the nucleus might be invoked to explain observable chemical changes was pointed out by two independent groups of workers.[41,42] They supposed that if the γ-ray energy were large enough, say 100keV., the daughter ^{80}Br nuclei would undergo recoil just as in the case of the (n, γ) reaction, which produces both isomers (as well as ^{82}Br from ^{81}Br). Alternatively, if the γ-ray energy were too small to give sufficient recoil to the ^{80}Br nuclei, it might be that instead of γ-ray emission the process of internal conversion was taking place, in which electrons from the *K* shell or, more rarely, from the *L* or even the *M* shell of the atom were ejected. In this case the momentum imparted to the recoil atoms would be considerably larger than if only a γ-ray were emitted. The energetics of this process have been discussed.[19,43]

The question soon arose as to whether the chemical effects noted by Segré, Halford and Seaborg, and also by De Vault and Libby,[41,42] could be quantitatively related to what was known about the ^{80m}Br transition. When the first chemical work was done, very little was known about the transition, but over the next few years both chemists and physicists were attracted by the problem. A good deal of confusion exists in the literature because both sets of investigators obtained mutually inconsistent results, and it seems best to deal briefly first of all with the physical evidence in historical sequence, and then to return to the chemical evidence mentioned above, following it through to the final resolution of the discrepancies.

PHYSICAL DATA ON THE ^{80m}Br → ^{80}Br TRANSITION

Electrons from internal conversion processes in ^{80m}Br were reported by workers using a magnetic β-spectrograph. At first they reported electron energies of 44 and 33·5 keV. and possibly a weaker line at 21·5 keV. Later these figures were slightly modified as more accurate experiments were made.[44] These results are shown in Table XV.

TABLE XV.- CONVERSION ELECTRON ENERGIES IN THE ^{80m}Br → ^{80}Br TRANSITION

Electron energy: keV.	Conversion in shell	γ-ray energy deduced: keV.
23·6	K or L_1	37·1 or 25·3
35·5	K	} 48·9 ± 0·4
47·2	L_1	

The uncertainty in the lower γ-ray energy arises from the fact that electrons of energy 23·6 keV. would be given either by a γ-ray of 37·1 keV. converted in the K shell, or by a γ-ray of 25·3 keV. converted in the L shell. Conversion of a γ-ray of 37·1 keV. in the L shell would unfortunately give an electron line indistinguishable from the K shell conversion line from the 48·9 keV. γ-ray. Nevertheless, it is clear from later work (see below) that the former alternative (a 37·1 keV. γ-ray) is the correct explanation.

Similar results were obtained by other workers using a similar technique. They reported that the most energetic line of electrons they observed corresponded with a γ-ray energy of 48 keV. and, moreover, that all the γ-rays were in fact converted.[45] However, experiments using a cloud-chamber at first put the highest energy γ-ray at 43 keV. with a conversion coefficient of only 0·3. Later the energy was amended to 47 keV. and the conversion coefficient to 0·43.[46] (Some confusion exists as to the definition of the term 'conversion coefficient'. It is here taken to denote the fraction of transitions of any one energy with which conversion electrons are associated, i.e. the ratio (number of conversion electrons)/(number of conversion electrons plus γ-rays)).

Meanwhile workers using Geiger counters and selective absorbers concluded that the decay scheme should be expressed in the following way: first of all the ^{80m}Br nucleus falls to a lower energy state by emission of an almost totally internally converted γ-ray of 48 keV., which is then followed by a second γ-ray in cascade of 37 keV., which is internally converted to the extent of about 0·50.[47]

Finally, experiments with coincidence counters were made, which confirmed the latter work and extended it as shown in Table XVI[48] (page 1123).

There is thus a great discrepancy between the observed total ratio of conversion electrons to 49 keV. transitions (a total of 1·0 to 1) compared with the cloud-chamber value (0·43), which undoubtedly reflects the difficulties, due to geometrical factors, in using the cloud-chamber as a 'counter' of nuclear events.

TABLE XVI. - CONVERSION COEFFICIENTS IN ^{80m}Br → ^{80}Br TRANSITION

γ-ray keV.	Proportion converted in K shell	L shell	Total internal conversion
49	0·88	1·12	1·00
37	0·34	0·05	0·39

CHEMICAL EFECTS OF THE ^{80m}Br → ^{80}Br TRANSITION

It is now clear from the physical evidence that a purely mechanical recoil mechanism cannot explain bond rupture, since the energy of the recoiling ^{80}Br atom, even assuming a 48 keV. conversion electron, is too small. If E_m is the energy of recoil in electron volts, E_e the electron energy in MeV. and M the atomic mass, it may be shown that

$$E_m = \frac{536E_e^2}{M} + \frac{541E_e}{M} = 0{\cdot}4\ \text{eV}.$$

This is, for example, less than one fifth of the C–Br bond energy.

It is convenient to consider the chemical experiments in order, taking the purely inorganic experiments first, and then those involving organic compounds.

In one investigation solutions containing ^{80m}Br as bromate ion were prepared, and to these were added, after different time intervals, solutions of bromide ion which was then precipitated with silver ion. The silver bromide separated showed the 18 minute decay ascribed to the daughter ^{80}Br. By noting the times between successive experiments and calculating the counting rate of the precipitate at the instant of formation, it was proved that the 18 minute body was being formed in the solution at a rate agreeing with that expected for the growth of an 18 minute daughter activity of a parent 4·4 hour activity. This separation of nuclear isomers and certain others, carried out independently and described later, using bromoform and also *tert.*-butyl bromide were the first to be reported by purely chemical methods.[42]

If a solution containing ^{80m}Br$^-$ in equilibrium with daughter ^{80}Br is placed in contact with finely divided silver chloride, the concentration of the daughter ^{80}Br in the solution adjusts itself to rather more than corresponds to radioactive equilibrium, while that on the surface of the silver chloride is correspondingly less. This is interpreted as indicating that some of the daughter atoms, upon formation from parent atoms adsorbed on the surface of the silver chloride, are ejected into the body of the solution and decay there before they can be re-adsorbed.[49]

If a mixture of gaseous bromine tagged with ^{80m}Br is mixed with hydrogen, the yield of H^{80}Br is effectively zero.[50]

From aqueous solutions of bromopentamminocobaltic ion and bromoplatinate ion containing ^{80m}Br the complexes may be precipitated as the nitrate and the ammonium salt, respectively, and the growth of 18 minute activity in the precipitates observed. The fraction of the ^{80}Br retained in combination in the complex ion in solution can thus be determined. Alternatively, the solid salts may be dissolved and immediately reprecipitated, the growth of the 18 minute activity again being followed, so that the fraction of ^{80}Br retained in the complex in the solid state can be calculated. The results of such experiments are given in Table XVII (see page 1124).

Clearly, with the cobalt complex in solution, all ^{80m}Br → ^{80}Br transitions remove the ^{80}Br atoms from the complex ions, but in the solid 14% of these re-enter the same, or other, complexes. With the platinum complex, however, this is not so; the percentage retention is probably not dependent on concentration of the solution, and in any case one would not expect re-entry at these

TABLE XVII. - RETENTION OF ^{80}Br IN COMPLEX IONS

Complex	Concentration	% Retention
$[Co(NH_3)_5Br]^{++}$	0·01 M.	0
$[Co(NH_3)_5Br](NO_3)_2$	solid	14
$[PtBr_6]^{--}$	0·00166 M.	52
	0·0005 M.	70, 53
	0·0005 M. with 0·003 M-NaBr	54
$(NH_4)_2[PtBr_6]$	solid	100

very low dilutions. Many more results with these, and other, complexes are desirable.[51]

In the first study of reactions involving organic compounds, 4·4 hour ^{80m}Br was made by neutron activation of ethyl bromide, and used with ordinary bromine carrier to synthesize *tert.*-butyl bromide. This compound was dissolved in aqueous methyl alcohol and then re-extracted from the solution with benzene. Bromine ion carrier was then added to the remaining aqueous phase and precipitated with silver ion. The precipitate showed an 18 minute decay, proving that isomer separation had occurred. It was pointed out at the time that the γ-ray emitted in the ^{80m}Br → ^{80}Br transition would almost certainly be much less energetic than that commonly found in (n, γ) reactions. Thus if the energy were of the order 100 keV., the recoil momentum given to the ^{80}Br nucleus would be insufficient to account for bond rupture. If, however, such a γ-ray were strongly internally converted, a K or L electron being ejected from the bromine atom, the recoil momentum from this would be much larger, so that chemical effects similar to those used in the Szilard-Chalmers techniques would be observed. As has already been remarked, the physical evidence finally rejects both these mechanisms.[41]

The foregoing report was followed immediately by another in which it was found that the lower active state (^{80}Br) activity could be precipitated with bromine ion carrier from bromate solutions containing $^{80m}BrO_3^-$, and also separated by extraction with water from bromoform containing $CH_3^{80m}Br$. These authors also explained their results by postulating a recoil effect from a highly converted γ-ray in the ^{80m}Br → ^{80}Br transition.[42]

An investigation has been made of the yield of ^{80}Br in water-soluble form produced by ^{80m}Br decay in ethylene dibromide mixed (after irradiation with neutrons) with 5% of aniline. The mixture was left before extraction long enough for all the initially-formed 18 minute activity to have decayed. Nevertheless, this activity was found in the aqueous extract, and by following the rate of re-growth of the extracted activity in the organic layers, the authors were able to calculate that about 90% of the transitions occurring in ethylene dibromide must lead to water-soluble bromine.[52] This figure is even higher than that quoted above for the yield of inorganic bromide, ^{80m}Br + ^{80}Br, formed by neutron capture in ethylene dibromide (59%).[15]

When gaseous hydrogen bromide (10 mm.) containing ^{80m}Br is mixed with acetylene (30 mm.) and allowed to decay partially, about 70% of the ^{80}Br daughter activity enters organic combination. This was shown by shaking the gaseous mixture with water and comparing the activities in the two phases.[28]

When bromine tagged with all three radioactive species, ^{80m}Br, ^{80}Br and ^{82}Br, is dissolved in carbon tetrachloride, only the ^{80m}Br enters the organic molecule, and moreover the rate of growth of activity (presumably $CCl_3^{80}Br$) is in accordance with its production from a 4·4 hour parent activity. The yield of organically combined ^{80}Br is between 30% and 40% of the rate of ^{80}Br production from ^{80m}Br. Studies of the reaction at different temperatures indicated that temperature has no certain effect, except that below the freezing point (experiments at -50° and -190°C.) the yield is only ~10%. It was pointed out that, although the recoil energy of the bromine molecule as the result of γ-ray emission corresponds to only 0·2 kg.-cal. per mole, the ejection of a conversion electron will give a recoil energy of about 3·7 kg.-cal. per mole. Neither figure is sufficient to account for interaction of the bromine atom and a carbon tetrachloride molecule. It was therefore suggested that conversion electron emission, followed by emission of *X*-rays and Auger electrons, might leave the bromine in an electronically excited state which enabled reaction to occur. Alternatively, free active bromine atoms might be formed with high kinetic energy.[50,52] It may here be explained that after the emission of a conversion electron, *e.g.* from the *K* shell, an electronic rearrangement in the atom is inevitable, the vacancy being filled by an electron from an outer shell, with the emission of a characteristic *X*-ray. Such an *X*-ray may be energetic enough to cause ejection of a further electron from, say, the outermost electron shell. This process is known as the Auger effect, and any ejected electron (after the original conversion electron) is referred to as an Auger electron. There would appear to be no reason, based on energetic grounds alone, why electrons involved in valency bonds in a compound should not take part in the process, in which case chemical reaction of some sort would always occur; on the other hand the observation that conversion electron emission is very often followed by chemical reaction does not necessarily prove that valency electrons are always directly involved in the Auger effect.

Further experiments, discussed in a second paper on this topic, concerned the reaction of bromine containing ^{80m}Br with carbon tetrachloride in the gas phase. The yield of organically-combined bromine was less than 2% over a range of temperatures (95° and 180°C.) and pressures (90 to 150 mm.). In other experiments ^{80m}Br was incorporated into cinnamic acid dibromide which was then dissolved in (liquid) carbon tetrachloride, when it was found that about 50% of the ^{80}Br daughter was substituted into the carbon tetrachloride. Other experiments which showed decomposition of gaseous ethylene dibromide (^{80m}Br) and substitution of bromine in mineral oil, were mentioned but not discussed in detail. The author made suggestions regarding the possible reaction mechanisms in which ^{80}Br might take part, including a consideration of the possible production of free radicals by secondary processes following ionization caused by the conversion electrons. It is, however, concluded that reaction cannot be expected in any case unless a conversion electron is emitted, and as the author was able to repeat the observations of others on the effect of added aniline, he concluded that the then currently accepted value of 0·3 to 0·4 for the conversion coefficient must be much too low.[50,54]

Experiments in which inactive tribromides of arsenic or antimony or phosphorus pentabromide were dissolved in neutron irradiated ethyl bromide, which had been kept long enough for the initially-formed ^{80}Br to have decayed virtually completely, showed that on volatilizing the organic bromide the residue of inorganic bromide carried an 18 minute activity, i.e. it had selectively exchanged with the ^{80}Br isomer. Similar results, but with a lower yield, were found for crystals of mercuric bromide and potassium bromide and for metallic silver, mercury and gold.

Again the difficulty of accounting for these reactions by a purely mechanical recoil mechanism is pointed out, even if allowance is made for conversion of the γ-ray. It was concluded that the process must involve some electronic rearrangement following loss of the conversion electron.[55]

In a series of thirty-two experiments measurements were made of the fraction of ^{80}Br daughter atoms escaping from their parent molecules under various conditions. Several organic bromides, and also bromate ion, were synthesized with ^{80m}Br, the daughter ^{80}Br being isolated in water-soluble form or precipitated as silver bromide. In no case was the yield greater than

95 ± 4%, for ethyl bromide in the gas phase, the next higher being 89 ± 4% for ethyl bromide in ethanol solution. In view of the picture which has been built up of the nature of the underlying nuclear and electronic processes, it is tempting to try to relate the chemical yields to the value of the conversion coefficient; in particular it seems reasonable that the latter should be at least as large as the fraction of the molecules reacting chemically, since this fraction may be depressed by the occurrence of recombination reactions. On this basis it appears immediately that the value of the conversion coefficient (0·43) deduced from the cloud chamber studies must be too low; at the same time the value of 1·00 from the absorption experiments is not quite convincingly confirmed either. It is clear from the experiment with ethyl bromide in the gas phase that bond rupture between the bromine atom and the rest of the molecule occurs in about 95% of all cases of activation; in the liquid and solid phases it is to be expected that some recombination would occur as the fragments of the molecule cannot easily move far from the site of the reaction, so that effective chemical yields of less than 95% are explicable. On the other hand recombination in the gas phase is hardly likely to be appreciable, so that if the true value of the conversion coefficient is 1·00 a maximum chemical yield of 100% should be realizable. It is difficult to say whether the discrepancy has any real significance.[56]

In a further and more detailed paper the same authors studied the extractability into aqueous solution of ^{80}Br from organic compounds containing ^{80m}Br, and found the upper limit to be 85%. One suggested explanation was that 15% of the upper state ^{80m}Br atoms decay by β-emission to the stable ^{80}Br. With the remaining 85% molecular breakdown occurs without exception because of loss of electrons due to the conversion process and the Auger effect. This 85% corresponds to the maximum chemical yields. Approximate calculations led the authors to conclude that in at least 15% of the conversion transitions all the valence electrons must be lost to the bromine atom; in more than 60% the loss is at least four electrons, less than 10% lose only two electrons, and less than 2% lose only one. It may be, however, that these two latter groups account for a substantial part of the 15% of unextractable bromine. At any rate, it seems plausible that the loss of so many electrons (at least three in 90% of the transitions) will lead to bond rupture. This may be regarded simply as a coulombic repulsion effect, the excess of positive charge distributing itself among different atoms in the molecule, or perhaps the process is more accurately described by saying that the bonds in the molecule cease to exist as the electrons constituting them are removed. The role played by the Auger effect in this connection has been given an approximate quantum mechanical treatment, showing that the ^{80}Br atoms might be expected to attain an average of 4·7 positive electronic charges.[57]

The experimental data obtained in this work may be summarised under three headings: (*a*) gaseous phase reactions, (*b*) extraction methods for ^{80}Br in liquid phase reactions, (*c*) capture of daughter ^{80}Br by organic molecules.

(*a*) Gas phase reactions were carried out with ethyl bromide (in one case with ethylene dibromide) synthesized with ^{80m}Br. In the first series, decay was allowed to proceed in the presence, and also in the absence, of water vapour, argon or air, after which the percentage of daughter activity removable into water (or in one case concentrated sulphuric acid), was determined. The average extraction was 55%. In a second series of experiments, with a much greater range of pressure of organic bromide, the non-organically-bound daughter ^{80}Br was extracted by vaporizing a small amount of inactive bromine into the gas phase and then spraying in a dilute aqueous solution of sodium sulphite. This reagent removed an average of 80% of the activity. The authors conclude that ^{80}Br atoms are formed in at least 80% of the transitions, but that some of these (about 25% of the total activity), while they will exchange with molecular bromine, are not extractable into water.

(*b*) In studying extraction methods for ^{80}Br in liquid phase reactions, experiments were carried out with ethyl bromide, 2:3-dibromopentane, *tert*-butyl bromide and bromobenzene, all containing ^{80m}Br, some in the pure state and others in mixtures with alcohol or carbon tetrachloride or both. The percentage of water-extractable ^{80}Br was lowered, other things being equal, by the presence of carbon tetrachloride, in confirmation of the earlier work already mentioned. The best yields of water-soluble ^{80}Br (89 ± 5%) were obtained from ethyl bromide (0·2 volume) in 95% ethanol (100 volumes), and from bromobenzene (1 volume) in 95% ethanol (100 volumes). These are somewhat larger than the yield of ^{80}Br precipitable as silver bromide from ^{80m}Br bromate solutions (66 – 80%). Solid ethyl bromide at −184°C. gave a yield of extractable ^{80}Br of 21%, compared with 43% for the liquid at 0°C., using water as the extracting agent; with bromine and bisulphite the extraction was 58%. This last observation confirms that made for the gas-phase reaction.

(*c*) To study the capture of ^{80}Br daughter by organic molecules, ^{80m}Br, as elementary bromine, was allowed to decay in solution in various mixtures of carbon tetrachloride and carbon disulphide. After a suitable interval the bromine was removed by shaking either with mercury or with aqueous sodium sulphite. The activity remaining in the organic layer was 34% for pure carbon tetrachloride and 9% for pure carbon disulphide, while mixtures of the two gave intermediate values. With mixtures of carbon tetrachloride and alcohol, the organically combined ^{80}Br fell from 34% (pure carbon tetrachloride) to 0·9% for 89 mole % ethanol with 11 mole % carbon tetrachloride.

An experiment was also carried out to see whether charged ^{80}Br atoms existed for appreciable times in ethyl bromide: a series of aluminium plates suspended 1·3 mm. apart in the vapour at 32·8 mm. pressure were charged alternately positive and negative with a potential difference of 103 volts. After four hours there was no detectable difference in the deposited activity on the several plates. This means either that equal numbers of positive and negative ^{80}Br ions must be formed, or that the charges must be neutralized by collision processes in which electrons are transferred in less than the collection time (about 10^{-4} second).

It has been suggested that the incompleteness of extraction of ^{80}Br by water, as compared with aqueous reducing agents, might be due to part, at least, of the daughter bromine remaining as single atoms rather than combining to give molecular bromine. This is perhaps not improbable when one considers the extreme dilution (10^{-13} molar, i.e. about 10^{8} atoms/cc., at which concentration even in the gas phase an atom undergoes only about two collisions per minute). If the activity were present as molecular bromine one would expect extraction into water to be complete owing to the hydrolysis

$$Br_2 + H_2O \rightarrow H^+ + Br^- + HBrO$$

which will be 99% complete for neutral bromine solutions less than 10^{-4} molar, or for acid solutions 10^{-9} molar. The possibility of the radioactive bromine being present in the molecular form may therefore be ruled out. It should however be noted that the presence of ordinary non-radioactive molecular bromine, present as an impurity at concentrations greater than those quoted, would have the effect of inhibiting complete hydrolysis of radioactive molecular bromine, since the two species although radioactively distinct are of course chemically identical. The authors reject this possible explanation also, at least as far as neutral solutions are concerned, on the grounds of their belief that the concentration of impurity molecular bromine could not have exceeded 10^{-6} molar.

An alternative hypothesis to account for the incompleteness of extraction by water is that the ^{80}Br might be present as free radicals such as CH_2Br.

It seems rather unlikely however that such radicals, or for that matter free bromine atoms, would be insoluble in water.[58]

The ideas then current about the chemical effects of the ^{80m}Br transition were discussed at the 21^{me} Congrès de Chimie Industrielle (Brussels, 1948). Some experimental work was described in which carbon tetrabromide was dissolved in ethyl bromide labelled with ^{80m}Br. After separating the two bromides, it was found that 20% of the daughter ^{80}Br atoms were substituted in the carbon tetrabromide. It was pointed out that there is a very close formal parallelism between the reaction mechanism to be expected assuming a 'recoil' process and that assuming that ^{80}Br atoms are produced with a high positive charge.[59]

A comparison has been made of the yield of organically combined radiobromine formed by the internal transition ^{80m}Br → ^{80}Br, with that formed by neutron activation of mixtures of bromine and tetrachloroethane and of bromine and carbon tetrachloride The results are shown in Table XVIII.

TABLE XVIII. - PERCENTAGE OF BROMINE WHICH ENTERS ORGANIC COMBINATION FOLLOWING NUCLEAR ACTIVATION

Phase	Activation	Concentration, or gas pressures	Yield of combined Br	
			with C_2Cl_4	with CCl_4
Solution	(n, γ)	0·7 mole % Br_2	37	24
Gas	(n, γ)	30 mm. Br_2 + 15 mm. C_2Cl_4	0	—
		60 mm. Br_2 + 60 mm. CCl_4	—	1·9
Solution	I.T.	0·1 mole % Br_2	85	34
Gas	I.T.	3 mm. Br_2 + 3 mm. C_2Cl_4	19	—
		100 mm. Br_2 + 700 mm. CCl_4	—	1·1

Other experiments showed that, while with neutron-activated bromine in carbon tetrachloride solution about 55% of the organically-combined bromine was found as trichlorobromomethane and the rest as higher-boiling compounds, the proportion as trichlorobromomethane from the internal transition reaction was about 70%, with the rest as higher-boiling compounds.

A study of the yield of organically-combined radiobromine as a function of the mole fraction of bromine in carbon tetrachloride showed that the curve of yield against mole fraction of bromine ranging from 0 to 1 was slightly convex to the origin.[32,50]

Experiments have been made on the electrodeposition on silver electrodes of radioactive bromine from neutron-irradiated ethyl bromide and ethylene dibromide. Without an electric field only the 4·5 hour period activity was detected, but when a potential of 115 volts/cm. was applied the 18 minute decay was observed in addition, on the anode.[31]

Electrodeposition studies have also been carried out using the Los Alamos 'water-boiler' as the neutron source for irradiation of butyl bromide. This was dissolved in 10 times its volume of acetone and silver plates 4 mm. apart were immersed in the solution. These were removed after 15 seconds, washed with acetone, dried and counted. They showed an 18 minute decay followed by a 4·5 hour decay, indicating an enrichment of the ^{80m}Br deposited. Other experiments with an electric field between the plates increased both activities on the anode.[60]

It is believed by some authors that the radioactivity acquired by silver electrodes immersed in neutron-irradiated organic bromides may be taken as a quantitative measure of their content of free, as opposed to organically-combined, radioactive bromine atoms.[61,62] This technique provides a very sensitive method for the detection of ^{80m}Br atoms in organic molecules, as a very high proportion of the daughter ^{80}Br atoms may thus be presented to a counting instrument in what is virtually a weightless source (with a silver backing). When neutron-irradiated ethyl bromide is mixed with inactive ethylidene bromide and the mixture separated again after a suitable interval, it is found that the ethylidene bromide as well as the ethyl bromide is brominated with ^{80m}Br atoms which in turn give free ^{80}Br atoms. This proves that bromination must occur in organic halides after irradiation ceases as well as during irradiation; assuming a unimolecular process, which seems reasonable since the organic halide molecules are always so greatly in excess, a figure of about 20 hours has been given for the half-period of this process. This 'subsequent synthesis' undoubtedly goes on also during the neutron irradiation, but is not itself sufficient (by a factor of the order of ten) to account for the rather high yields of combined ^{80m}Br usually found (68% in a typical 4·5 hour bombardment of ethyl bromide; calculated yield from subsequent substitution process 7%).[63]

In further experiments by one of the same authors ethyl bromide was irradiated alone and also mixed with five times its volume of lead tetraethyl; then the irradiated pure ethyl bromide was mixed with lead tetraethyl, and both mixtures were fractionally distilled to obtain pure fractions of ethyl bromide. The free radiobromine content of both samples was measured by the electrodeposition technique and the complex decay curves were resolved. While the activities of the 4·5 hour half-life and the 34 hour half-life were nearly identical, the 18 minute activity was found to be five times as great in the pure ethyl bromide target as it was in the mixture. Since sufficient time (2 hours) had elapsed after irradiation for all the originally formed ^{80}Br to have decayed, about five times as many ^{80m}Br atoms must have been formed in the pure ethyl bromide irradiation as in the mixture, owing presumably to the experimental impossibility of ensuring the same bombardment intensity of the target liquids because of their difference in volume and chemical nature. Since only about the same number of free ^{80m}Br atoms (and ^{82}Br atoms) were found in the two cases, it must follow that recombination reactions during irradiation were more efficient, by a factor of about 5, in the pure liquid than in the mixture.[64]

That the chemical nature of the target compound has an influence on recombination during and after irradiation, was shown by experiments on ethyl bromide, ethylene dibromide, and bromoform. The total activity obtainable by neutron irradiation of equal volumes of these compounds (correcting for radioactive saturation) was proportional to the number of bromine atoms per cc. of liquid (approx. 1 : 1·75 : 2·56), but the number of free radiobromine atoms obtainable from irradiated ethyl bromide was about ten times that obtainable from bromoform.[65]

Further experiments with the homologous series from methyl bromide to *n*-hexyl bromide showed that there is an increase in 'subsequent synthesis' effects as one passes up the series, but superimposed on this general tendency there is a very marked 'odd-even' effect, molecules with odd numbers of carbon atoms giving much greater yields of free radiobromine (^{80m}Br and ^{82}Br) than their neighbours on either side.[66]

It has been stated that ^{80}Br is collected on the anode when gold electrodes are immersed in bromobenzene previously irradiated with slow neutrons. The efficiency of this process must, however, be less that 100%, as it was shown that the ratio of ^{80}Br to ^{80m}Br formed during neutron irradiation of bromobenzene is greater than the relative amounts anodically deposited, after making due allowance for the transition of some of the ^{80m}Br into ^{80}Br during the irradiation and the electrolysis itself. Thus whatever the efficiency of collection of ^{80m}Br (which may or may not be 100%), the efficiency of collection of ^{80}Br is somewhat less.[34]

When ethyl bromide labelled with ^{80m}Br is agitated for half an hour with the exchange resin Amberlite IR4B, some separation of the bromine isomers may be effected.[67]

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The efficiency of bond rupture in the ^{80m}Br → ^{80}Br transition has been examined in experiments using ^{80m}Br combined in methyl bromide. After allowing decay to proceed for a short time, the vapour was very quickly pumped through a soda-lime trap to remove free bromine and hydrogen bromide, and then condensed on a 'cold finger' trap surrounding a counter. Experiments both with and without added inactive hydrogen bromide showed that there was a scarcely detectable retention of the 18 minute activity in the methyl bromide. The conclusion reached is that there can no longer be any doubt that bond rupture does occur in essentially all cases of ^{80m}Br decay. That this does not seem to happen in liquid reactions can only be due to recombination reactions of some sort which are inhibited in the gas phase by the ready escape of the freed bromine atoms from the rest of the molecule.[68]

The electric charge on ^{80}Br atoms formed in the transition from ^{80m}Br has been deduced from measurements of the activities deposited on electrodes in gaseous ethyl bromide labelled with ^{80m}Br. It was concluded that rather more than 50% of the ^{80}Br atoms are positively charged and the rest are neutral.[69] This is to be compared with the rough calculation that at least 98% of the ^{80}Br atoms should be positively charged.[58]

Unsuccessful attempts have been made to find by chemical means whether the ^{80}Br excited atoms formed in liquid ethylene dibromide containing $C_2H_4^{80m}BrBr$ were present as bromide ions or as neutral atoms or molecules. These experiments did, however, show that the effects of temperature and change of phase on the production of substitution products noted with the propyl bromides are paralleled with ethylene dibromide.[70]

The yield of organically-combined ^{80}Br in bromotrichloromethane labelled with ^{80m}Br has been studied over a wide range of temperature. The yield increases slightly as the temperature is lowered from room temperature to the melting-point (-5°C.), at which temperature it increases abruptly; a further gradual increase is observed in the solid phase down to -80°C. The actual figures are given in Table XIX.[39]

TABLE XIX. - ORGANIC YIELD OF ISOMERIC TRANSITION BROMINE IN CCl_3Br

Temperature, °C.	25	0	-8	-80	-190
Organic yield, %	54	63	70	86	87

The electrodeposition of ^{80}Br atoms formed from ^{80m}Br in ethyl bromide has been studied, using electrodes thin enough to be used as the windows of Geiger-Müller counters. In this way the activity of the deposit was measured continuously during electrolysis. It was found that at first the 18 minute bromine was collected exclusively at the anode, but after about 10 min. the reverse was the case. The explanation of this phenomenon is that the liquid at first contains negative ions, such as inactive Br$^-$, which may be present either as impurities or produced by ionization processes during the neutron bombardment. Then, whatever the initial charge of the excited ^{80}Br atom immediately on formation, they can undergo charge exchange to become ^{80}Br$^-$, and will be collected on the anode. When, however, all the negative ions have been collected, the excited ^{80}Br atoms must remain in their original state of charge, and this is shown to be positive by their collection at the cathode.[71]

CHEMISTRY OF BROMINE FORMED BY β-DECAY OF SELENIUM

Experiments have been made to determine the state of oxidation of ^{84}Br (30 min.) and of ^{83}Br (2·4 hours) formed by β-decay of ^{84}Se (25 min.) and ^{83}Se (2 min.), the selenium being present in aqueous solution as selenite or as selenate ion. In view of the exchange reactions undergone by elemental bromine, it was possible to distinguish only between a 'reduced form' (i.e. Br , Br_2, BrO^-) and bromate. Table XX gives the results obtained.[72,73]

TABLE XX. - PERCENTAGE OF BROMATE FORMED IN β-DECAY OF SELENIUM

Isotope and chemical form	Carriers present	pH	Bromate %
^{83}Se, SeO_3^{--}	SeO_3^{--}, BrO_3^{--}	7·0	38 - 42
^{83}Se, SeO_3^{--}	SeO_3^{--}, BrO_3^{--}	7·2	30 - 56
^{84}Se, SeO_3^{--}	SeO_3^{--}, BrO_3^{--}	7·2	51
^{83}Se, SeO_4^{--}	SeO_4^{--}, BrO_3^{--}	7·0	39
^{83}Se, SeO_3^{--}	None	6·6 - 7·0	26 - 53
^{83}Se, SeO_3^{--}	None	10·6 - 11·2	24 - 30

IODINE

With iodine consideration must be given to the reactions of ^{128}I (25 min.) formed by slow neutron capture in the stable isotope ^{127}I, and also to the reported production of ^{132}I (2·4 hours) in the β-decay of ^{132}Te (77 hours).

CHEMISTRY OF ^{128}I PRODUCED BY SLOW NEUTRON CAPTURE IN ^{127}I

When solid sodium iodate, or periodate, is irradiated with slow neutrons and then dissolved in water, a large proportion (70 - 90%) of the induced activity follows the chemistry of iodide ion or iodine being co-precipitated with silver iodide.[13,14]

In other experiments it has been confirmed by precipitation and counting of lead iodate that the rest of the activity remains as iodate ion.[9] The first report on ^{128}I, however, is the well-known note by Szilard and Chalmers[1] to which reference has already been made. These authors irradiated ethyl iodide with slow neutrons and found that a very large proportion of the radio-iodine could be extracted with aqueous solutions of iodide ion. Many workers later confirmed this fundamentally important observation.[74]

That the radio-iodine formed in organic halide irradiations is largely in the ionized state (I^-) was shown by experiments with smooth copper electrodes dipping into the liquid during irradiation, the radioactivity being collected on the anode. The effect was shown for the following liquids: methyl iodide, ethyl iodide, butyl iodide, methylene di-iodide and iodobenzene.

There seems little doubt that the essential process involved is the presence in the liquid of iodide ion with which the newly-formed ^{128}I atoms could exchange. If special precautions are taken to remove all ions initially present, *e.g.* by electrolysis of the liquid before irradiation until its conductivity falls to zero, it is found that no activity can be deposited on either electrode after irradiation. On the other hand, if 'zero conductivity' ethyl iodide is so treated as to produce iodine atoms in it, the effect of collection of ^{128}I on the anode reappeared. Such treatments were, e.g., standing in sunlight for several days, passing hydrogen iodide into the liquid, or adding a little iodine followed by sulphur dioxide. In one experiment the radioactive iodine collected was 100% of that formed. The effects of stirring and of using other electrodes, i.e. platinum and silver, were investigated briefly.[27]

Substitution reactions similar to those found for chlorine and bromine also occur in organic iodide irradiations. Thus when methyl iodide is irradiated, both at room temperature and at -195°C., 11% of the radio-iodine is found as methylene di-iodide, the remainder being about equally distributed between a water-soluble fraction and methyl iodide. In these experiments, aqueous solutions of iodide containing sulphur dioxide were used as the extractant. When solutions of iodine in ethyl alcohol are irradiated, small yields are obtained of radioactive methyl and ethyl iodides. Solutions of iodine in acetic acid also give radioactive methyl iodide. An irradiated mixture of methyl iodide and benzene gave a 15% yield of radioactive iodobenzene. Radioactive methyl iodide may be prepared by passing air saturated with the vapour through irradiated solutions of iodide ion in acetic acid.[16,75]

Various techniques designed to give almost carrier-free activities of the water-soluble radio-iodine have been devised. The percentage of the total activity which may be obtained from ethyl iodide in this way appears to be less than when a carrier is used, but very high specific activity of the irradiated liquid may be achieved. Some authors have used pure water for the extraction of irradiated ethyl iodide,[17] but better results have been obtained using aqueous hydrogen sulphide, which gives an enrichment factor greater than 10^6,[76,77] and by adsorption on to active charcoal[18,78] for which an enrichment factor of about 10^8 is claimed. There is some doubt, however, whether such extremely high enrichment factors can really be achieved since some radiochemical decomposition of the target liquid by the γ-ray flux and by ionization caused by knock-on protons which are inevitably present in practice, invariably leads to the production of free inactive halogen atoms. Nevertheless, solutions of radio-iodine have been obtained so dilute as to give no visible precipitate of silver iodide.

For other organic iodides, the presence of free halogen molecules in the irradiated liquid has no marked effect in increasing the yield of extractable radio-iodide. Thus in Table XXI results are given for this yield, expressed as a percentage of total activity formed, when the following pre-treatments were given to the target liquid before irradiation: (*a*) none, (*b*) washing with aqueous thiosulphate, (*c*) addition of 1-3% free iodine.

TABLE XXI. - EFFECT OF FREE HALOGEN ON THE YIELD OF EXTRACTABLE RADIO-IODINE FROM IRRADIATED ORGANIC HALIDES

Target compound	Pre-treatment	% activity extracted by 5% sodium thiosulphate
n-Butyl iodide	a	56
	b	47
	c	55
Iodobenzene	a	30
	b	39
	c	36

The effect of adding small amounts (4%) of aniline before the irradiation is to increase the yield of radio-iodine extractable into aqueous media in one case studied, although the effect was not observable in others, as is shown in Table XXII (see page 1133).

It seems curious that the increased extractability caused by the presence of aniline should be so much more clearly observed with chlorine and bromine isotopes than with iodine.[15]

The effect of dilution of the target liquid with a liquid not containing halogen has been studied by several authors. Thus it is found that when pure iodoform is irradiated with slow neutrons and then dissolved in alcohol, about 40% of the radio-iodine may be obtained in aqueous solution, whereas if the target is a 1·1 mole per cent solution of iodoform in pyridine the proportion extractable into aqueous media rises to 99%.[9] In some experiments

TABLE XXII. - EFFECT OF ADDED ANILINE ON THE EXTRACTABILITY OF RADIO-IODINE FROM IRRADIATED ORGANIC HALIDES

Target liquid	Added substance	Extracting reagent	Mean % extracted
n-Butyl iodide	none	5% HCl	11
	4% aniline	5% HCl	44
	none	5% $Na_2S_2O_3$	47
	4% aniline	5% $Na_2S_2O_3$	45
Iodobenzene	none	5% HCl	10
	4% aniline	5% HCl	8
	none	5% $Na_2S_2O_3$	30
	4% aniline	5% $Na_2S_2O_3$	31

it was found that some radioactive iodine remains in organic combination; thus with iodoform about 60% of the activity is retained and with ethyl iodide 37%. On the other hand irradiation of iodine solutions in pentane produces radioactive amyl iodides, the yield varying in different experiments between 23 and 38%.[79]

A method has been worked out whereby the radio-iodine extracted from ethyl iodide may be co-precipitated with silver iodide and the count obtained used to indicate the strength (in arbitrary units) of the neutron flux employed. The ethyl iodide is either irradiated in the pure state and then extracted with 0·03% potassium iodide solution, or it is irradiated with a little dissolved iodine (0·005 g.I/litre) and extracted with sodium sulphite solution. In the former procedure 58·9 ± 3·6% of the active iodine is extracted; in the latter 64·3 ± 3·0%. The difference between these figures is explained by assuming that in the iodine-solution procedure iodine may inhibit the exchange reaction:

$$^{128}I^- + C_2H_5{}^{127}I \longrightarrow {}^{127}I^- + C_2H_5{}^{128}I$$

by means of the reaction

$$^{128}I^- + {}^{127}I_2 \rightleftharpoons {}^{127}I^- + {}^{127}I^{128}I$$

the latter reaction being purely an exchange process occurring with thermal or near-thermal iodine atoms, as distinct from the unidirectional reaction,

$$^{128}I(\text{recoiling}) + {}^{127}I^{127}I \longrightarrow {}^{127}I^{128}I + {}^{127}I.$$

The authors claim that by their method neutron fluxes may be compared with an error of about ± 0·5%.[80]

Further work on the production of radioactive organic halides has been reported briefly whence it appears that slightly higher yields (by about 5%) are obtainable from dilute solutions of ethyl iodide in various hydrocarbons than from iodine itself in the same hydrocarbons. This difference may be due to the operation of one or other of the following effects: (*a*) the iodine atoms in the solutions of iodine may be in large colloidal aggregates rather than as I_2 molecules, so that a considerable fraction of the ^{128}I atoms formed may be reduced to nearly thermal energies by collisions within the aggregate before they escape from it and have a chance to react with the organic molecules; (*b*) the presence of iodine molecules in the iodine solution may reduce the concentration of hydrocarbon radicals formed by collision processes with energetic ^{128}I atoms; (*c*) the presence of iodine molecules in the iodine solutions may give rise to exchange processes which have the effect of replacing some ^{128}I atoms by inactive ^{127}I atoms. All these suggested mechanisms tend to reduce the chance of synthesis of radioactive organic halide.

CHEMISTRY OF IODINE FORMED BY β-DECAY OF TELLURIUM

The yield of ^{132}I, formed by decay of ^{132}Te from tellurite and tellurate solutions 0.1 N. in HNO_3, which is obtained in a reduced state (I^- or I_2) and as iodate and periodate, has been studied and the results are given in Table XXIII.[72,73]

TABLE XXIII. - DISTRIBUTION OF ^{132}I IN DIFFERENT VALENCY STATES FROM ^{132}Te DECAY

Chemical form	Percentage yield from	
	Tellurite ion	Tellurate ion
Reduced state (I^- or I_2)	75	60
Iodate	14	28
Periodate	11	12

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